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Chemical, Physical and Hazards Properties of Quadricyclane

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NOTICE

FOREWORD

The work reported in this special report was performed under JON: 10110046. The project manager at OL–AC PL/RKFE Branch of the Phillips Laboratory (now the Air Force Research Laboratory, Propulsion Directorate, Edwards Facility), Edwards AFB CA 93524–7680 was Dr. Patrick G. Carrick.

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13. ABSTRACT (MAXIMUM 200 WORDS)
Theoretical predictions have identified quadricyclane, a liquid hydrocarbon, as a possible replacement for, or additive to, the current kerosene-based rocket propellant RP-1. Density, viscosity, thermal conductivity, heat capacity, flash point, purity, 90-day aging, high temperature decomposition, impact sensitivity, friction sensitivity and detonation sensitivity (card gap) have been studied. In-depth studies on the thermal decomposition and rapid compression heating were performed by NASA White Sands and are included in this report. Taken as a whole, the results indicate that quadricyclane can be easily handled as a liquid propellant fuel and should have performance advantages over RP-1. However, since the performance and physical properties of quadricyclane differ from RP-1, implementation of quadricyclane may require some modification of current propulsion hardware.

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Glossary

Abbreviation	Description
AL	Armstrong Laboratory
ARC	Accelerated rate calorimetry
b.p.	Boiling point
DSC	Differential scanning calorimetry
GC	Gas chromatography
HEDM	High Energy Density Matter
LN_2	Liquid nitrogen
m.p.	Melting point
MS	Mass spectrometry
NPN	n-propyl nitrate
PETN	Pentaerythriol tetranitrate
PL	Phillips Laboratory (now Air Force Research Laboratory)
UV	Ultraviolet light
WSTF	White Sands Test Facility

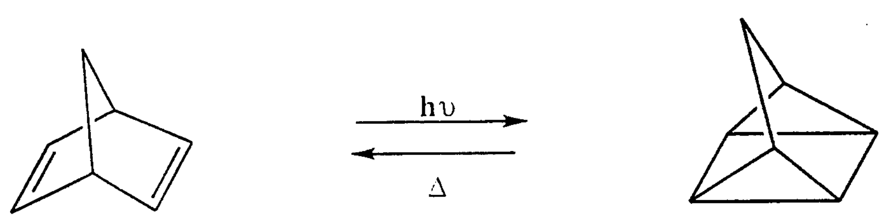
1. SUMMARY

Theoretical predictions have identified quadricyclane, a liquid hydrocarbon, as a possible replacement for, or additive to, the current kerosene-based rocket propellant RP-1. Density, viscosity, thermal conductivity, heat capacity, flash point, purity, 90 day aging, high temperature decomposition, impact sensitivity, friction sensitivity and detonation sensitivity (card gap) have been studied. In-depth studies on the thermal decomposition and rapid compression heating were performed by NASA White Sands and are included in this report. Taken as a whole, the results indicate that quadricyclane can be easily handled as a liquid propellant fuel and should have performance advantages over RP-1, however, since the performance and physical properties of quadricyclane differ from RP-1, implementation of quadricyclane may require some modification of current propulsion hardware.

2. INTRODUCTION

Theoretical predictions have identified the hydrocarbon quadricyclane as a possible replacement for, or additive to, the current kerosene-based rocket propellant (RP-1). Quadricyclane offers the advantages of increased performance and density over RP-1 while it is environmentally "friendly" compared to other energetic fuels such as hydrazines. Under the High Energy Density Matter (HEDM) program at Phillips Laboratory research has been conducted to fully characterize the quadricyclane compound. We have examined the chemical composition, physical properties (density, viscosity), heat transfer properties (melting point, boiling point, heat capacity, and thermal conductivity), hazards (flash point, impact, friction, detonation sensitivity and rapid compression) and material compatibilities (90 day aging, 150°C hot tube).

Quadricyclane is a strained ring hydrocarbon (Fig. 1). It has a molecular formula of C_7H_8 with a formula weight of 92.14 g. The precursor to quadricyclane is norbornadiene, which is also a C_7H_8 compound. Quadricyclane is synthesized through photolysis using UV or visible light[1-4]. It is known to react when exposed to acids[2], certain metal complexes[5] or heat[2,5].



Norbornadiene (Bicyclo[2.2.1]hepta-2,5-diene)

Quadricyclane (Tetracyclo[$2.2.1.0^{2,5}.0^{3,6}$]heptane)

Figure 1
Synthesis of Quadricyclane

Our study was carried out in support of 1000 lbf engine test firings performed at Phillips Laboratory, Edwards AFB CA in August and September 1995. Studies on the toxicology (AL/HSC, Armstrong Laboratory/Occupational & Environmental Health Directorate, Wright-Patterson AFB OH) and environmental fate (AL/EQ, Armstrong Laboratory/Environics Directorate, Tyndall AFB FL) of quadricyclane[6] are also under way. Portions of this report[7] have been communicated earlier.

3. EXPERIMENTAL

Three lots of Quadricyclane were obtained. The first from Aldrich Chemical Co., followed by 10-kg and 45-kg lots from EniChem America. All three were screened for purity. The Aldrich material and the 10-kg EniChem lot were used for laboratory testing while the 45-kg EniChem lot was used primarily for rocket engine firings.

3.1 Quantitative Analysis

Determination of the purity of quadricyclane samples was carried out using gas chromatography (GC). We used a Hewlett-Packard 5890 gas chromatograph with a 7673A automatic sample injector and a 3396A automatic integrator. The capillary column used for this analysis was a HP Ultra Performance capillary column, methyl linked methyl silicone (HP-1), 25 m x 0.31 mm x 0.52 µm. Other instrument test parameters are found in Table 1. Representative GC traces of quadricyclane and a RP-1/quadricyclane mix are found in Figures 2 and 3.

Table 1. Gas Chromatography and Integrator Parameters for Quantitative Analysis

Chromatograph Parameters		Integrator Parameters
initial temp 30°C	equil 1.0 min	zero = 0
initial time 5.0 min	air flow 450 cc/min	att2^ = 6
rate 50 deg/min	H2 flow 60 cc/min	cht sp = 1.0
final temp 275°C	aux air 30 cc/min	ar rej = 10,000
final time 8:00 min	head pressure 17.5 psi	thrsh = 4
inj temp 200°C	split flow 120 cc/min	pk wd = 0.4
det temp 225°C	column flow 6 cc/min	

3.2 Density

The density of the pure quadricyclane and mixed quadricyclane/RP-1 samples was analyzed on an A.P. PAAR DMA 48 density meter, which determines the density of liquids and gases by measuring changes in the period of oscillation of the sample cell. The measuring range of the instrument is 0 to 3 g/cm^3, accuracy $\pm 1 \times 10^{-4}$ in the range of ± 0.5 g/cm^3 around a calibration point, sample size approximately 0.7 cm^3 and the temperature range -10.0 to +70.0°C with an accuracy of 0.1°C. The instrument was calibrated at each temperature prior to use. Air and water were used as calibration standards. A fresh sample was used for each measurement at a given temperature. The density at each

temperature was measured twice, once for each ascending (e.g., 10°C to 70°C) temperature followed by a measurement made for each descending (e.g., 70°C to 10°C) temperature.

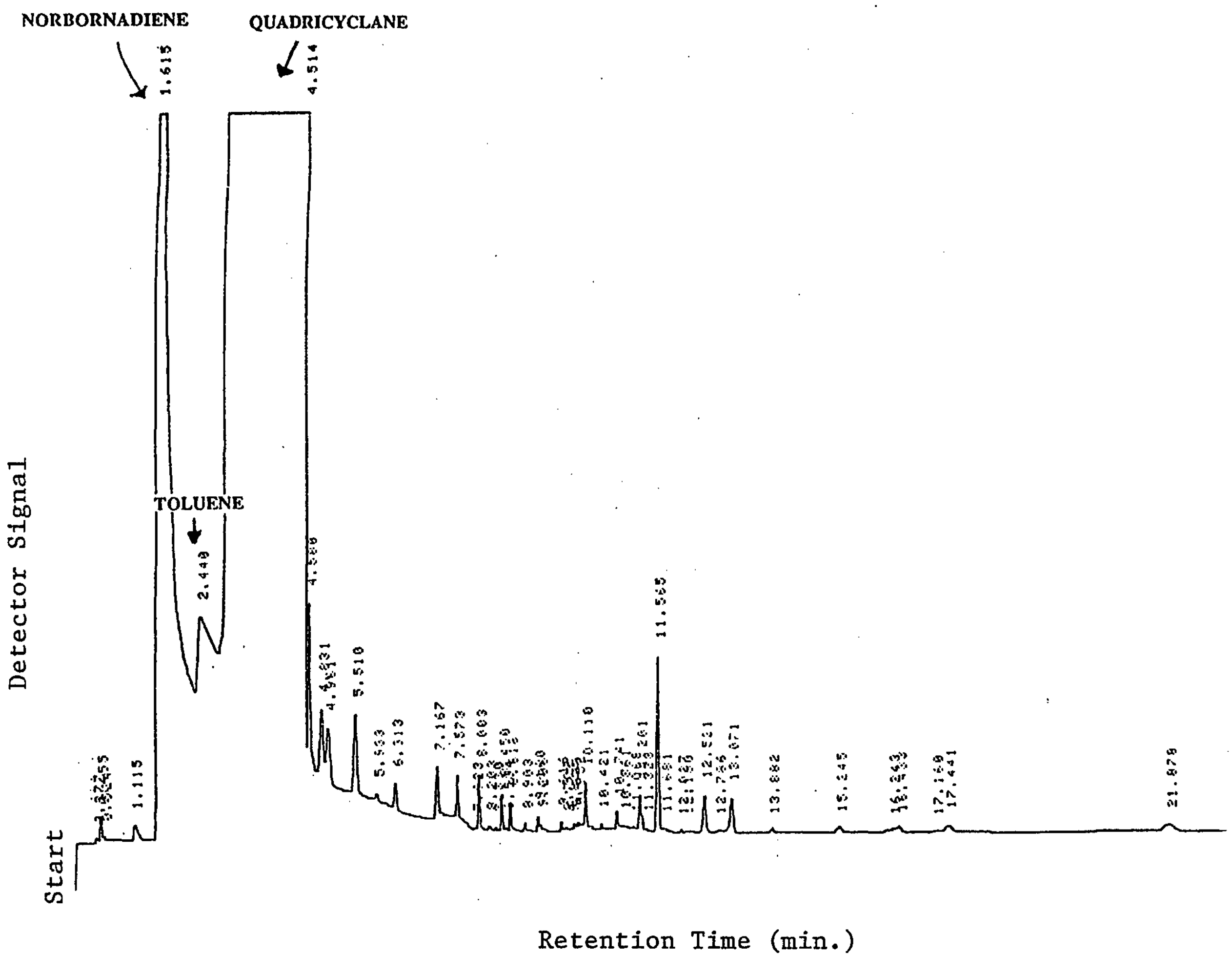


Figure 2
Gas Chromatograph And Peak Integration Of Quadricyclane

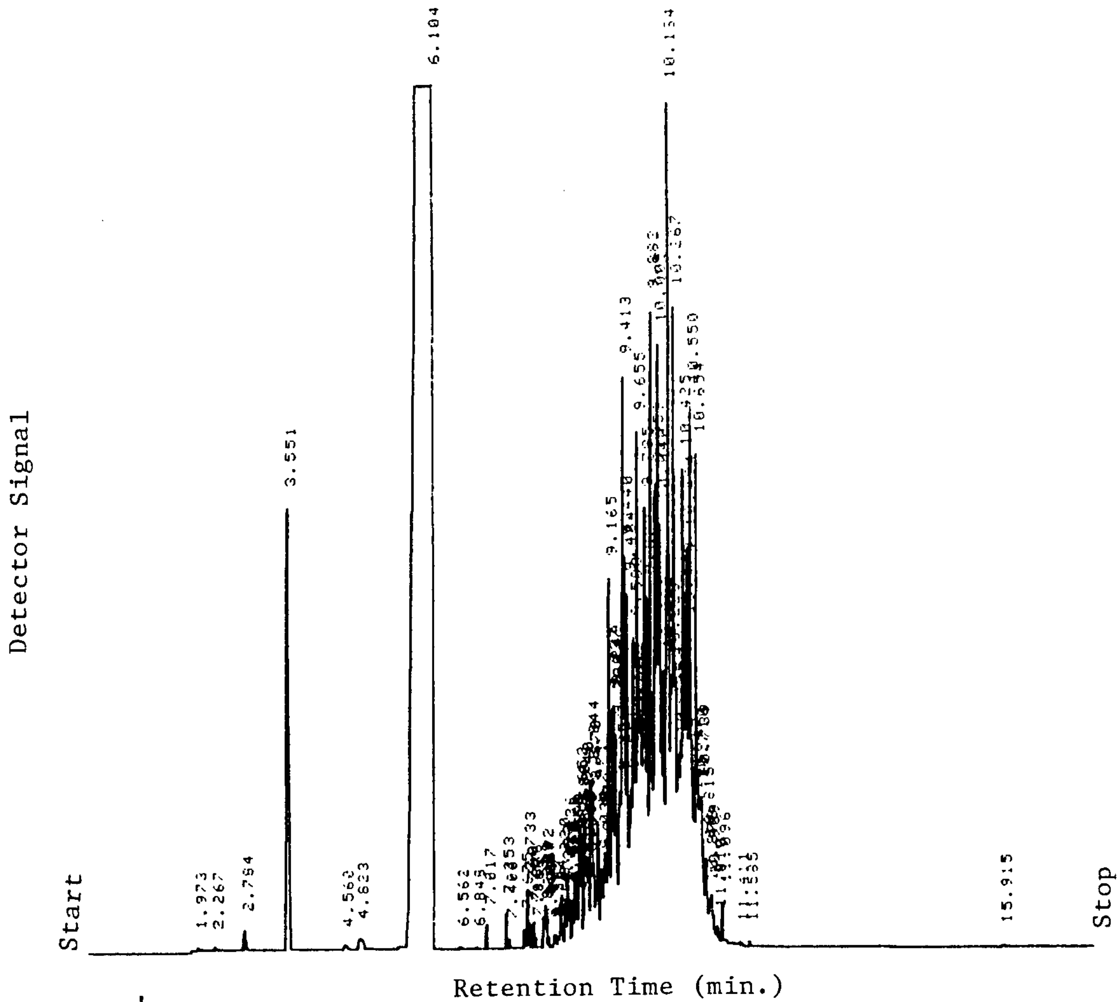


Figure 3
Gas Chromatograph and Peak Integration of RP-1/Quadricyclane

3.3 Viscosity

The viscosity values for quadricyclane were determined using an AVS 410 Schott Automatic Viscometer. Methods ASTM D445 and ASTM D446 were used for this analysis. The viscometer tubes were calibrated with Cannon Certified Viscosity Standards conforming to ASTM Oil Standards. Two standards were used to cover the temperature range: 1) Viscosity Standard N1.0, Lot #94101, to cover temperatures between 20°C to 40°C, viscosity tube (Kimax size 50, A66), giving a constant value of 0.00335 and 2) viscosity Standard S20, Lot #95301, viscometer tube (Kimax size 25, G54), for temperatures between 50°C to 80°C, giving a constant value of 0.0014937. Tabulated values represent the average of three consecutive measurements for a sample.

3.4 Differential Scanning Calorimetry

Thermal properties (boiling point, melting point and heat capacity) were determined on a DuPont Instrument 910 Differential Scanning Calorimeter (DSC). The

instrument was calibrated in both the temperature and heat flow modes using indium and sapphire materials respectively. Hermetic aluminum pans were used as sample holders in the analysis. The DSC apparatus was purged with nitrogen at a flow rate of approximately 50 ml per minute throughout the experiment.

Phase transitions were examined by first cooling the sample cell to -150°C, holding isothermal for 10 minutes, then ramping at a rate of 10°C/min. to 200°C, and again holding isothermal for 10 minutes. The data were reduced by determining and integrating the apex of each peak or phase transition.

Heat capacity was determined using Test Method ASTM E-1269. Test runs of three analyses were taken in duplicates: a steady-state isothermal baseline, reference using sapphire, and the test sample of quadricyclane. The test started at -100°C, held isothermal for 10 minutes, the temperature was then ramped at a rate of 10°C/min to 100°C holding isothermal for 10 minutes. The analysis was repeated three times to achieve accuracy and repeatability. The data was reduced by determining the temperature value needed versus heat capacity.

3.5 Thermal Conductivity

Determination of thermal conductivity was performed at The Institute for Research, Houston, TX. Methods used for analysis were ASTM E-1225 and D2717-Guarded Hot Plate Method. The material (quadricyclane) was analyzed over a temperature range from -40°C to 100°C. Their report is included as Appendix A.

3.6 Flash Point

The flashpoint for quadricyclane was measured with a Pensky-Martens semi-automatic apparatus using the ASTM D93 method. Approximately 60 cc of the material was placed in the steel cup to the level indicated by the filling mark. The lid was placed on the cup and the cup was set into a liquid nitrogen (LN_2) bath to bring the liquid to approximately -20°C. The cup was then removed from the LN_2 bath and placed on the apparatus stove (however, the stove was not needed to heat the sample). Ambient room temperature warmed the liquid at a rate of 2°C/min. The test flame was lit and the sample mixture was stirred at a downward direction. As the temperature increased a degree or every few degrees, the test flame was lowered into the vapor space of the liquid for 1 second and then quickly raised to the starting position. The temperature was recorded as the flash point at the time the test flame application caused a distinct flash on the interior of the cup. The test was repeated five times using a fresh sample for each analysis.

3.7 Material Compatibility

3.7.1 <u>90-Day Aging.</u> Examinations were made of quadricyclane and quadricyclane/RP-1 mix (50:50) when exposed to various materials under conditions expected for normal loading and storage. Test materials were each submerged in glass scintillation vials containing 20 ml of quadricyclane or quadricyclane/RP-1 and enclosed with Teflon™ seal caps. Materials remained submerged for the 90-day duration of the analysis. Sample vials were limited to filtered light at room temperature under nitrogen (with the exception of the air samples). [The air samples were filled with 10 ml of each

liquid and held outside the nitrogen environment. One day each week, the vials were exposed to the atmosphere for 5 minutes.] Two vials of each fuel/material combination were prepared. Each vial was monitored weekly. Visual inspections were made to check for color changes and flocculation - quadricyclane is reported to polymerize when in contact with air[7]. The composition of each vial was also monitored by GC. Approximately 1 ml from each sample vial were transferred to GC vials and analyzed in duplicate.

3.7.2 Hot Tube. Ten ml of liquid fuel is placed, under nitrogen, in a glass pressure tube (Fisher-Porter) along with a small sample of the compatibility test material. The tube is then closed and submerged for 10 minutes in a preheated oil bath. A GC is taken before and after each test to monitor compatibility.

3.7.3 Accelerated Rate Calorimetry (ARC). The ARC investigation of quadricyclane with copper NarloyZ was performed by NASA at their White Sands Test Facility using a Columbia Scientific Instruments Co. calorimeter. Specific information on the experimental procedures is included in the NASA report included as Appendix B

3.8 Detonation Sensitivity

3.8.1 Impact/Drop Weight Test. The machine used for this test was an Olin Mathieson, Model 7, made by Technoproducts. The test method to perform this analysis was also developed by Technoproducts. A small sample of approximately 0.03 cc of quadricyclane was enclosed in a cavity of 0.06 cc formed by a steel cup, an elastic O-ring, and a steel diaphragm. A piston rests on the diaphragm and carries a vent hole which is blocked by the steel diaphragm. A weight is dropped onto the piston. Explosion is indicated by puncture of the steel diaphragm, accompanied by a loud noise. The sensitivity value for a given sample is the potential energy value (height x weight) at which the probability of explosion is 50 percent. Machine calibrations were made using n-propyl nitrate (NPN) and water.

3.8.2 Friction Test. The apparatus used to determine the sensitivity of a substance to friction was a Julius Perters Model 21. For this analysis, porcelain plates (25 mm x 25 mm x 5 mm thick) were used. A sample size of 30.0 microliters of quadricyclane was spread onto a porcelain plate. In accordance with the test procedure, the top porcelain plate is held at a starting weight of 37.8 kg, at a distance of 30.0 cm out from the stationary arm length. The bottom plate that holds the sample contains the moveable arm. The apparatus is actuated by pressing the starter button in which the two porcelain plates are rubbed together. For each load, the test was performed six times. The test was evaluated by listening for a "crackling" noise and by looking for "sparks" due to the rubbing of the plates or by looking for "charring" on the plates, or "no reaction".

3.8.3 Card Gap Test. Approximately 39 cc of liquid sample was placed in a steel cylinder tube 1 1/2-in. i.d. X 5 1/2 in. deep. A donor charge of two penolite pellets (2 in. diameter by 1 in. long), blasting cap, a steel plate (6 in. x 6 in. x 18 in. thick), and cards composed of cellulose acetate. The sample analyzed was loaded into the cylinder. The cellulose cards (if necessary), were placed on top of the loaded cylinder between the sample and donor charge. The sample cylinder was then placed on top of the steel plate and lit in a contained and controlled pit. This test was performed three times per sample

using water as a negative test, pentaerythriol tetranitrate (PETN) for a positive test and lastly, the test sample, quadricyclane.

3.8.4 Rapid Densification. Rapid compression (also known as adiabatic compression or water hammer tests) were performed by NASA personnel at their White Sands Test Facility. In this test quadricyclane was compared with hydrazine, known to detonate under these conditions. NASA's findings and their test procedures are included as Appendix C.

4. RESULTS AND DISCUSSION

Quadricyclane was originally identified as a potential rocket propellant ingredient based on its chemical formula (C_7H_8), heat of formation[6] ($\Delta Hf = +72.2$ kcal/mol), density[7] (0.985 g/cc) and availability from a convenient source (Aldrich Chemical Co.). Between these simple, first-cut considerations and actual implementation in a flying propulsion system are many tests, evaluations and decisions. To support this process, especially the firing of a 1000 lbf engine we examined a broad spectrum of physical and chemical properties of commercially available quadricyclane samples. Our objectives were to obtain and tabulate data to support the testing and to evaluate available materials to identify possible problems or issues pertinent to quadricyclane's eventual implementation in a flight weight propulsion system.

4.1 Composition, Purity and Quantitative Analysis

Gas chromatography is the ideal method for analyzing the composition and purity of volatile hydrocarbon liquids. Figures 2 and 3 are sample GC traces of quadricyclane from EniChem America and a blend of quadricyclane with RP-1. The compositions for the two samples are listed in Table 2. Spiking the sample with a small quantity of the suspected impurity or combined GC/MS analysis verified the identification of minor impurity species. The small research-quality sample from Aldrich was 99+% pure while the sample from EniChem was 95% quadricyclane. Norbornadiene, the starting material for quadricyclane production, was the major impurity identified. Cycloheptatriene and toluene were other impurities. These impurities could have been present in the starting materials used to produce the quadricyclane, or they could have been produced during quadricyclane production, or they could be products of slow decomposition of the quadricyclane during storage and shipping. The traces of $C_{14}H_{16}$ species detected in both samples were apparently from dimerization of the quadricyclane. Both samples had also been treated with antioxidant stabilizers. The Aldrich material had 0.01% $C_{15}H_{24}O$ identified by GC/MS as BHT while the EniChem sample has 0.1% $C_6H_6O_2$ identified as CATACHOL. GC analysis was used throughout the study to monitor sample purity and to verify the composition of blends.

Table 2. Composition of Quadricyclane Materials from Various Suppliers

Compound	Aldrich	EniChem 10-kg and 45-kg lots
Quadricyclane	99.506	95.725
Norbornadiene	0.312	3.527
Toluene	0.085	0.233
Cycloheptatriene	0.002	0.122
Dimer	0.008	0.034
Stabilizer	0.010	0.10

4.2 Density

Accurate knowledge of propellant density is required for vehicle, tankage, turbopump and injector design. Ground operations, vehicle performance and payload rating also depend on a reliable value of the propellant density. Since the various vehicles or subsystems may have different ambient or operational temperatures, density must be accurately known over a range of temperatures. Ideally, the density of a propellant would be high (e.g., > 1.0 g/cc) - facilitating a compact vehicle design - and be a slowly varying function of temperature - minimizing the potential errors in adjusting for various ambient and operational temperatures.

Table 3 and Figure 4 show our results for the various quadricyclane samples while Table 4 shows the values for RP-1/Quadricyclane blends. Figure 5 compares quadricyclane with RP-1.

Table 3. Density of Quadricyclane (g/cc)

Temperature (°C)	Aldrich	EniChem (Small can)	EniChem (45 kg drum)
10.0	0.9944	0.9897	0.9894
15.0	0.9894	0.9848	0.9844
20.0	0.9875		0.9787
25.0	0.9796	0.9750	0.9746
30.0	0.9743	0.9698	0.9693
35.0	0.9692	0.9647	0.9642
40.0	0.9642	0.9597	0.9592
50.0	0.9537	0.9493	0.9487
60.0	0.9435	0.9390	0.9384
70.0	0.9332	0.9288	0.9281

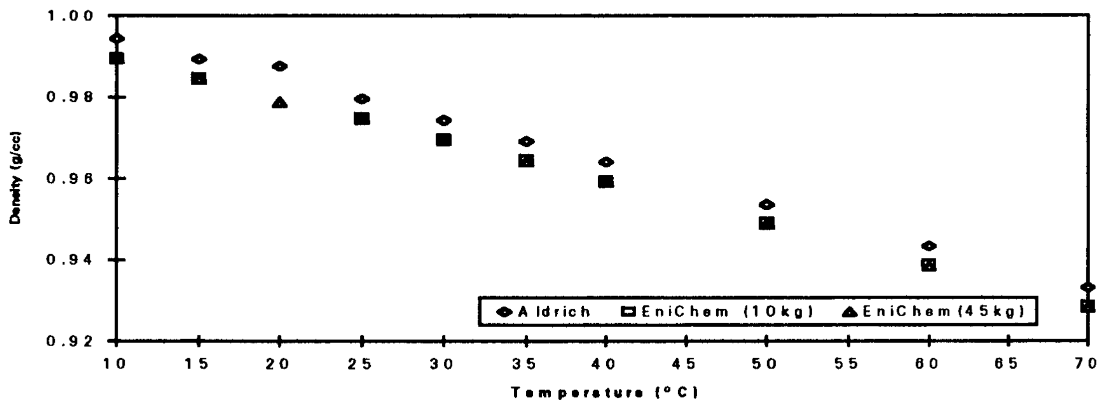


Figure 4

Comparison of Densities of Quadricyclane from Various Suppliers

Table 4. Density of RP-1/Quadricyclane Mixtures[a] (g/cc)

	RP-1 / Quadricyclane Ratio[a]				
Temperature (°C)	**100/0**	**75.2/24.8**	**51.9/49.1**	**25.5/74.5**	**0/100**
10.0	0.8075	0.8475	0.8870	0.9359	0.9897
20.0	0.8032	0.8395	0.8783	0.9261	0.9791
30.0	0.7960	0.8316	0.8699	0.9174	0.9696
40.0	0.7914	0.8264	0.8644	0.9110	0.9625
50.0	0.7814	0.8156	0.8529	0.8986	0.9490
60.0	0.7714	0.8077	0.8444	0.8891	0.9388

a. Ratios are by weight RP-1/Quadricyclane.

The data indicates that quadricyclane is considerably denser than the kerosene based RP-1 (0.98 vs. 0.80 at 20°C) - a reflection of both the compact strained-ring structure of quadricyclane and the low hydrogen content of the molecule. While the increased density makes quadricyclane generally more desirable as a propellant, Figure 5 indicates that the density of quadricyclane is a stronger function of temperature than RP-1. This aspect of the material is less desirable than RP-1 and could require more accurate temperature measurements in storage tanks and engine components to insure that mass and volume of quadricyclane is properly interconverted.

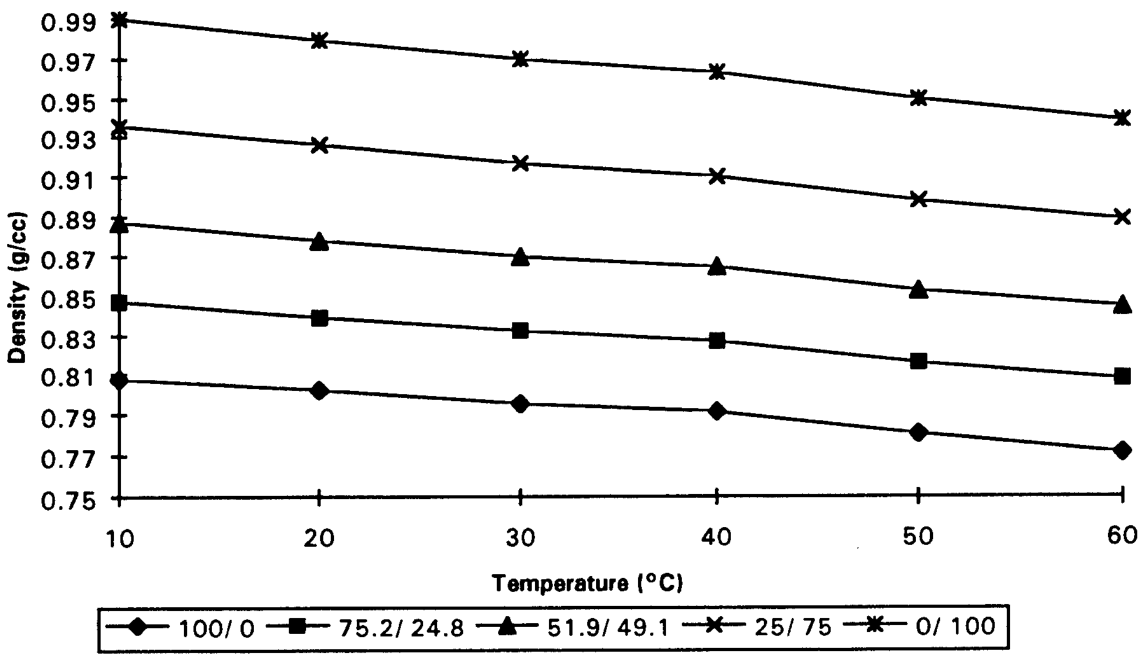


Figure 5
Comparison of Densities of Various RP-1/Quadricyclane Mixtures

4.3 Viscosity

The viscosity is an important pumping property for fluid flow calculations in an engine, particularly the turbopumps. The viscosity of quadricyclane is recorded in Table 5 and plotted versus temperature in Figure 6. A plot of ln(viscosity) vs. 1/T is linear as expected[8] (see Fig. 7).

Table 5. Kinematic Viscosity of Quadricyclane at Various Temperatures

Temperature (°C)	Viscosity (centistokes)
10.0	1.2212
20.0	1.0614
30.0	0.9372
50.0	0.7465
60.0	0.6745
70.0	0.6177
80.0	0.5715

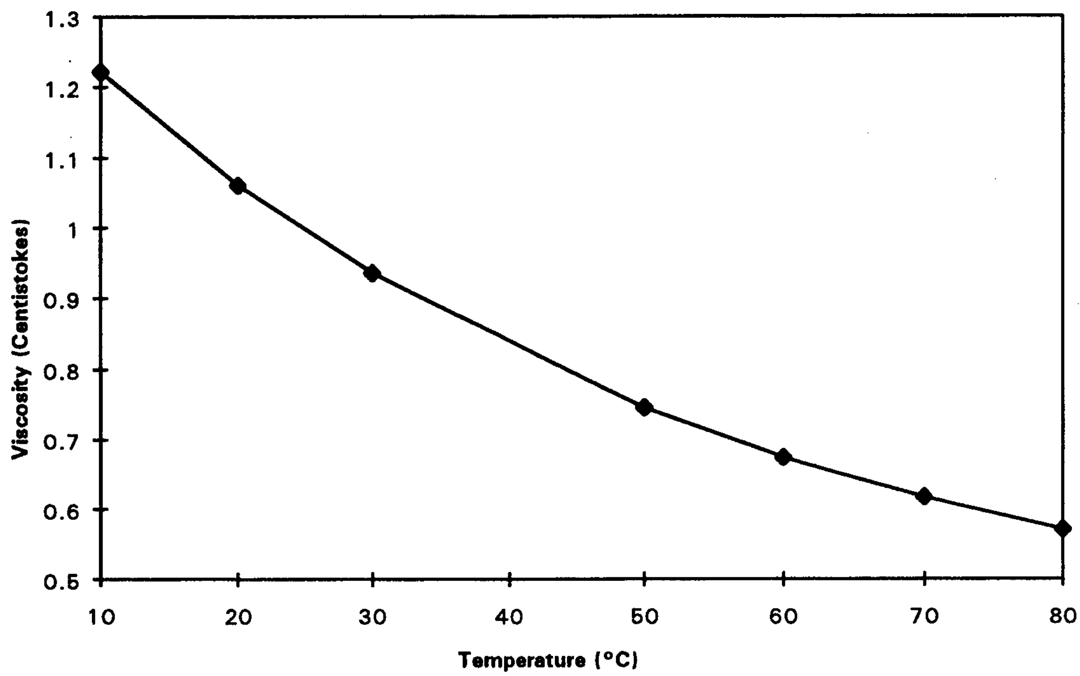


Figure 6
Kinematic Viscosity of Quadricyclane at Various Temperatures

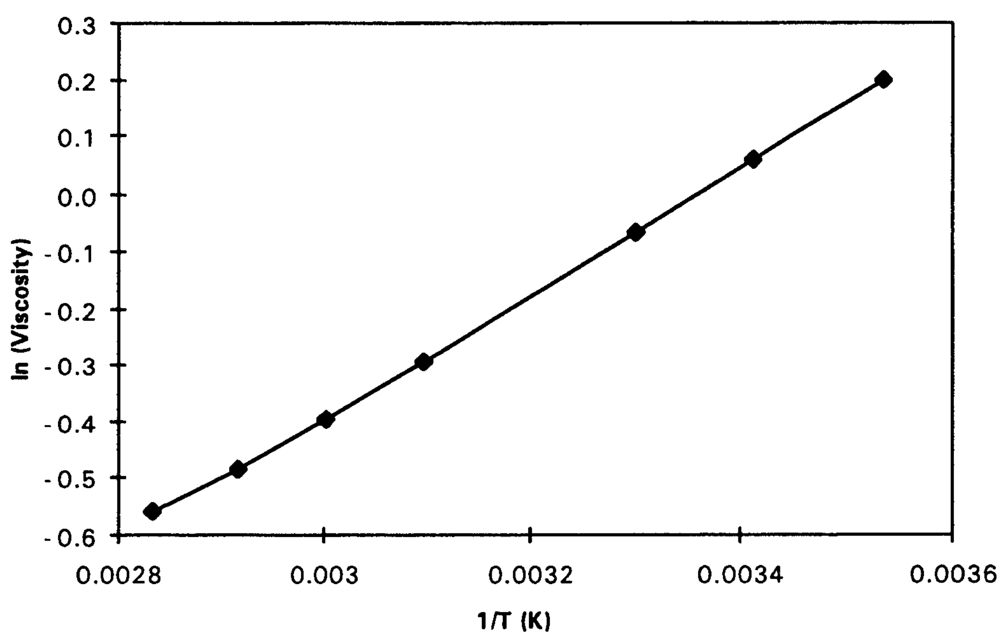


Figure 7
ln(Viscosity) versus I/T

The values for viscosity of quadricyclane are less than viscosity values for RP-1 over the same temperature range (RP-1 = 20 centistokes @ 20°C)[9]. However, this should not pose a significant problem for ground operations or turbo-pumping. For example, at 20°C, the viscosity of quadricyclane is about the same as that for hydrazine (0.91 centistokes)[9], a common propellant.

4.4 Phase Transitions and Heat Capacity

The boiling point (b.p.) and melting point (m.p.) of quadricyclane were determined by DSC. A sample trace is shown in Figure 8. Based on this scale, the boiling point of quadricyclane was found to be 107.68°C while two other phase transitions were detected at -89°C and -44°C. After further analysis of a frozen sample of quadricyclane at ≈-50°C, the melting point was confirmed to be -44 °C. This low melt is desirable for operating at low temperatures. The phase transition detected at -89°C, may be due to a possible crystal lattice rearrangement which merits further research.

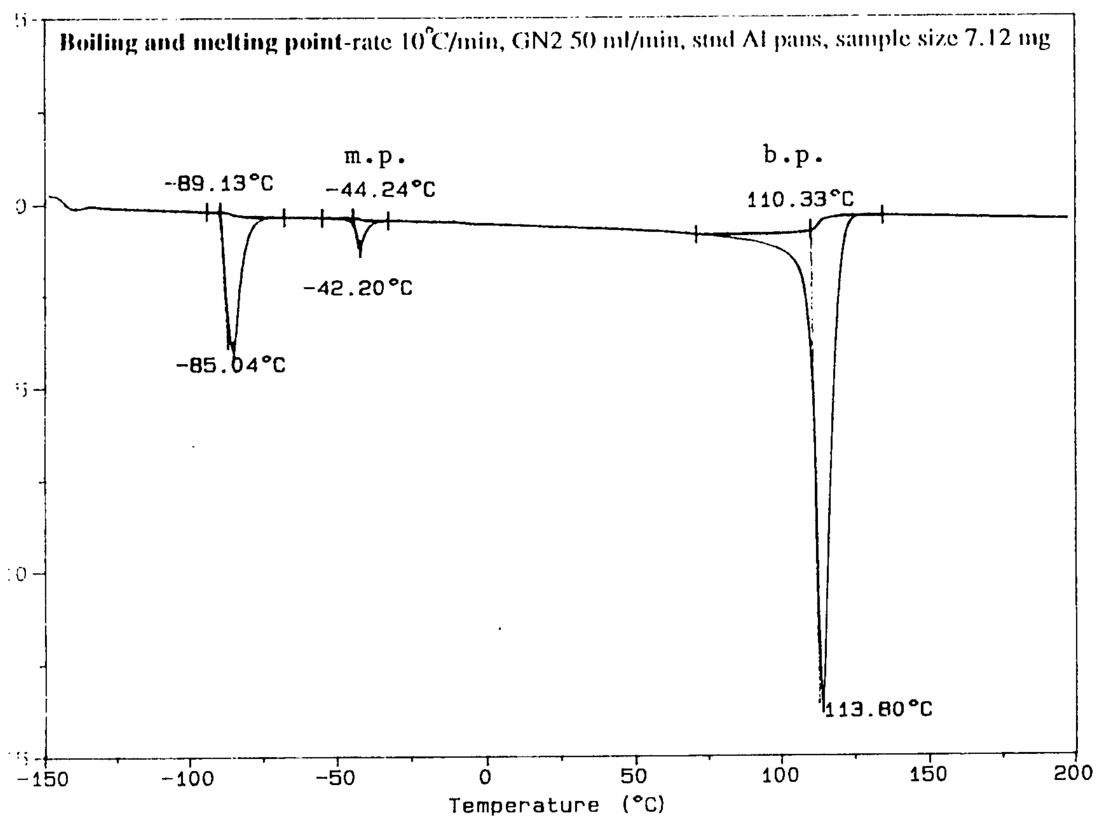


Figure 8
DSC Behavior of Quadricyclane

The heat capacity (Cp) of quadricyclane measured versus temperature (°C) is plotted in Figure 9. From this plot we derived a value of 1.664 J/g°C at ≈ 25°C. This is similar to the value reported by Steele et al. (1.65 J/g, Ref. 6) and somewhat lower than the heat capacity value of the standard rocket fuel, RP-1 (1.88 J/g°C at ≈ 25°C)[9].

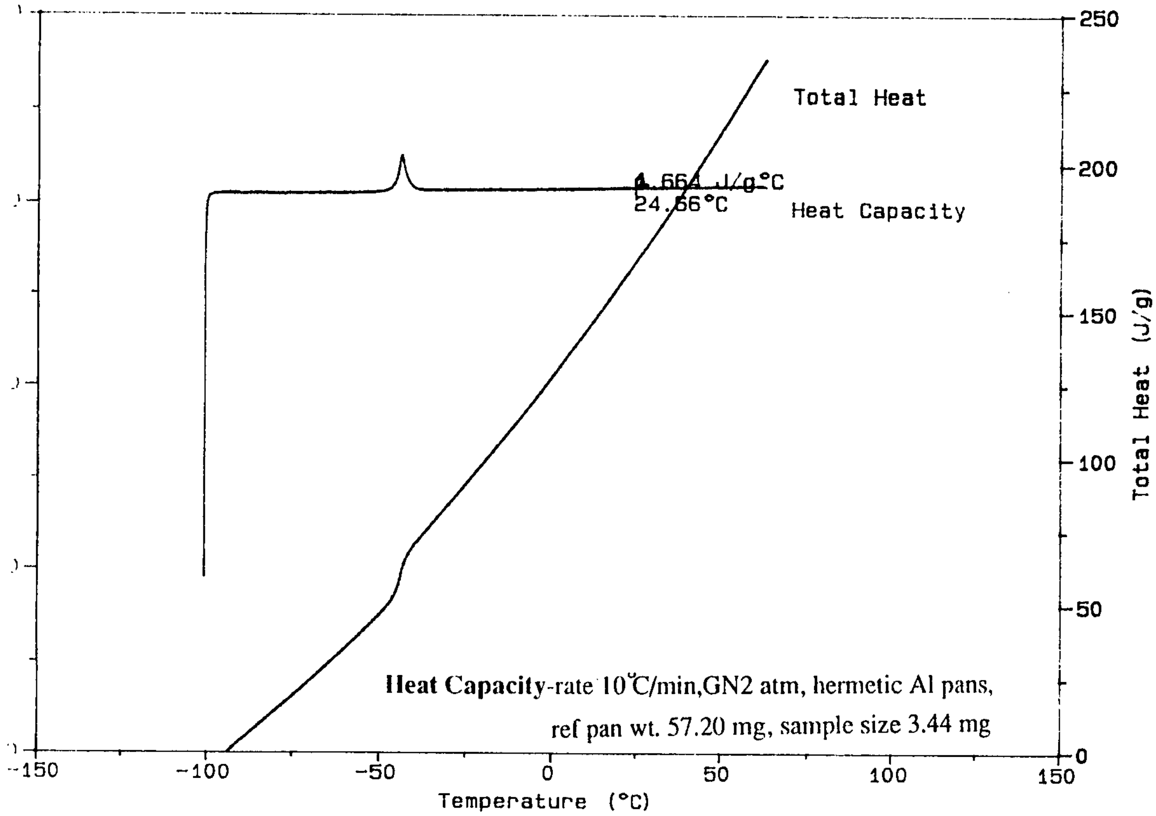


Figure 9
Heat Capacity of Quadricyclane

4.5 Thermal Conductivity

Table 6 lists the results of the thermal conductivity study performed at The Institute for Research, Houston, TX. As with other properties, quadricyclane differs from RP-1, but again the differences are small and should not present a great obstacle to quadricyclanes application as a rocket propellant. The variation of thermal conductivity with temperature is larger than the variation for RP-1. Again this is not a desirable feature, but it is not a "show-stopper".

Table 6. Quadricyclane Thermal Conductivity (cal sec^{-1} cm^{-1} $°C^{-1}$)

Temperature (°C)	Quadricyclane (EniChem)	RP-1*
-40.0	0.000397	0.000339
-10.0	0.000379	0.000331
20.0	0.000352	0.000327
50.0	0.000325	0.000323
80.0	0.000312	0.000318
100.0	0.000284	0.000310

* Reference 9

4.6 Flash Point

The manufacturers report a flash point of 11°C for quadricyclane and -11°C for norbornadiene. The coincidence of ±11 degrees for the two compounds was somewhat suspicious. We have independently measured +2°C for the EniChem materials. Regardless of the exact value, these fuels are obviously very easily ignited under normal conditions in air and are justifiably classified as FLAMMABLE LIQUIDS for shipping and handling. RP-1 has a flash point of 57°C and is classified as a COMBUSTIBLE LIQUID.

4.7 Material Compatibility

4.7.1 90-Day Aging. Since quadricyclane has a large positive heat of formation, we were concerned that small amounts of impurities or exposure to various materials during storage may lead to decomposition - possibly even to a "thermal runaway" reaction where decomposition was actually heating the bulk material and feeding an accelerating decomposition. To get some grasp on this problem, two sets of tests were set up, 90-day aging and hot tube decomposition.

In the 90-day aging test portions of quadricyclane or quadricyclane/RP-1 (50/50) were stored in glass ampoules along with small samples of contaminants or structural materials. The materials chosen for study were: Viton, 304 stainless steel, rust, tap water and air. Specimens were monitored weekly for color change, precipitate formation and composition (GC). The results are summarized in Table 7. A sample of the GC results for the apparently nonreactive combination of 304 stainless steel in pure quadricyclane is shown in Figure 10. Only one test showed a decrease in quadricyclane composition. One sample vial of the mixture of quadricyclane/RP-1 50/50 exposed to air showed a decrease of quadricyclane from 53% to 45% over the study period (Fig. 11). A second similarly prepared vial did not show any change in concentration.

Table 7. 90-Day Aging Analysis

Material	Pure Quadricyclane	50/50 Quadricyclane/RP-1
Control	No Change	No Change
Viton	No Change	No Change
304 Stainless Steel	No Change	No Change
Tap water	No Change	No Change
Air	No Change	-9% in one vial No Change in 2nd Vial
Rust	No Change	No Change

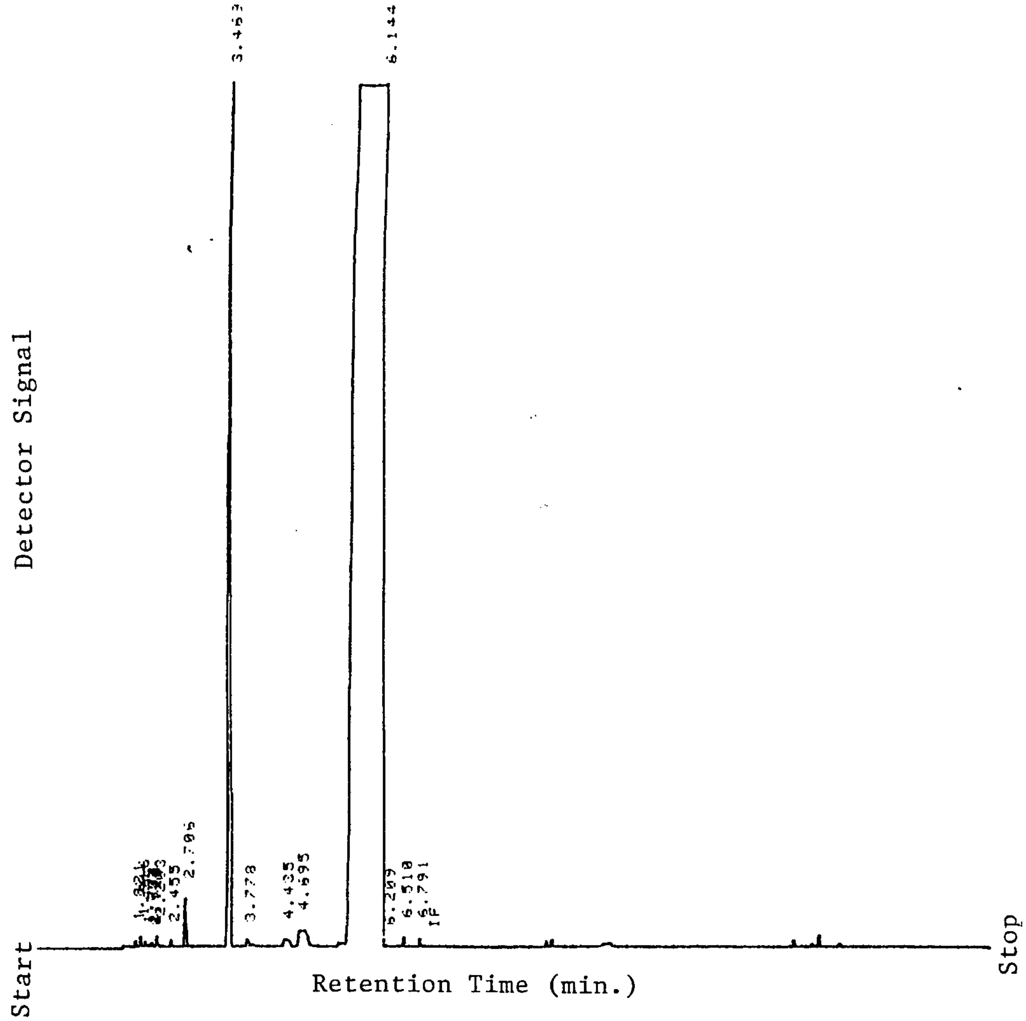


Figure 10
GC Trace of Quadricyclane Exposed to 304 Stainless Steel over 90 Days

The test results indicate that quadricyclane and quadricyclane/RP-1 blends can safely be stored for moderate amounts of time if efforts are made to exclude air and light. The manufacturer stabilized the quadricyclane used in these tests against oxidation and polymerization with catechol. We did not add any further stabilizers. We could not monitor the fate of the stabilizer or predict how long it might be effective. The one test which did show appreciable decomposition was a blend of quadricyclane with RP-1. It is possible that some component of the RP-1 is responsible for accelerated reactivity in the presence of air. Alternatively, something in the RP-1 may react with and deplete the stabilizer in the quadricyclane, rendering the material susceptible to air oxidation or polymerization.

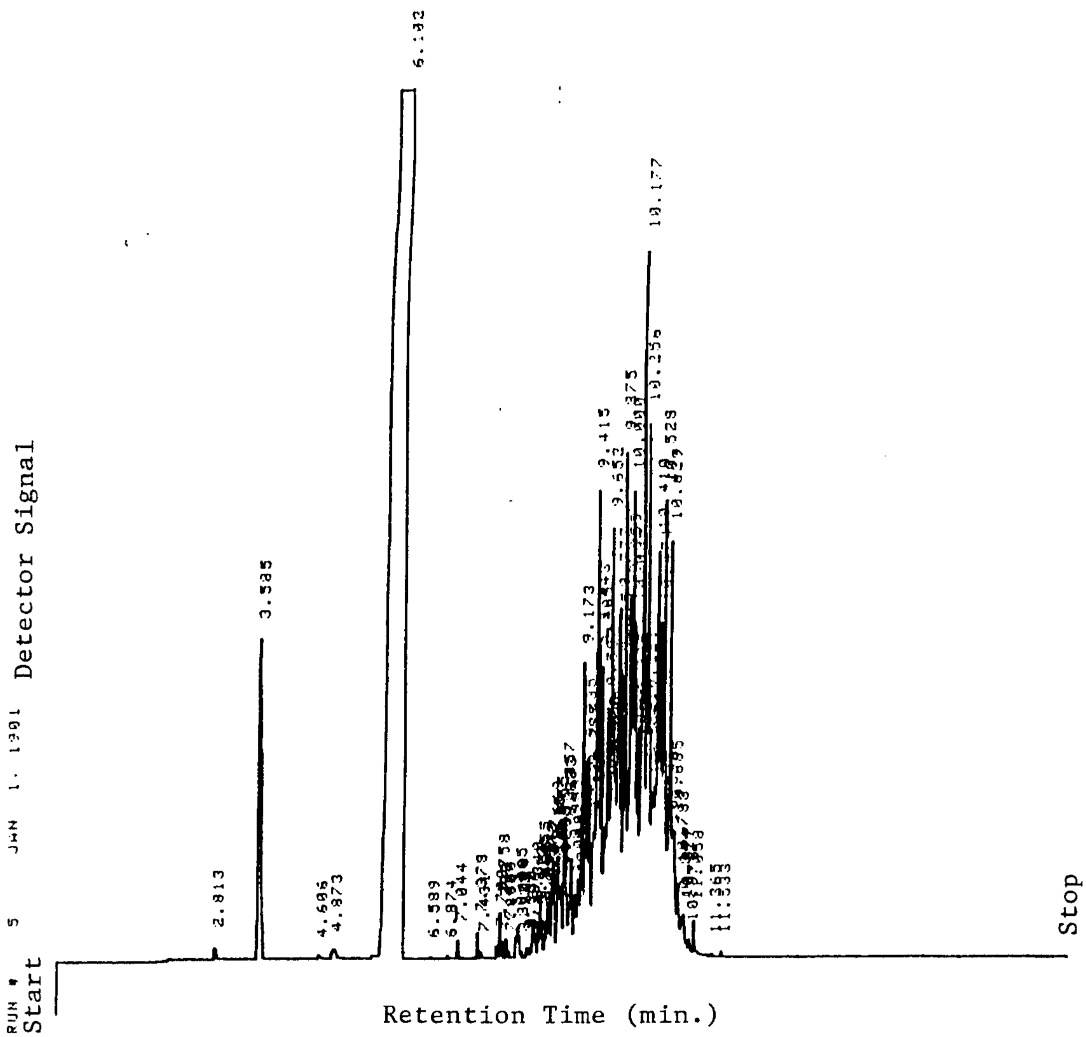


Figure 11
GC Trace of RP-1/Quadricyclane (50/50) Exposed to Air over 90 Days

4.7.2 Hot Tube Test. The hot tube test was conducted to determine if decomposition, self-heating, or thermal runaway can be induced when quadricyclane (or RP-1/ quadricyclane) comes in contact with various materials at high temperatures. This attempt was to mimic the conditions which may briefly exist when fuel is pumped through a hot, firing rocket engine as a coolant before it is injected into the combustion chamber (regenerative cooling). The metals/materials tested were: blank (control), copper, aluminum, Stainless Steel 4130 and Stainless Steel 316, Viton, rust and water. Table 8 shows the test matrix and our observations. The test conditions of minimum 150°C for 10 minutes are hotter and longer than would be expected for a normal regenerative cooling residence. We were most interested in finding conditions where the material greatly

accelerated the decomposition over that observed for the blank. Only copper seemed to pose any risk of such an acceleration, and this effect was small.

Table 8. Hot Tube Material Compatibility

Quadricyclane Concentration	Material (heated at 150°C)
	Blank (control)
no change	Aluminum
(decreased) -1.35%	Copper NarloyZ
no change	Rust
no change	Stainless Steel 4130
no change	Stainless Steel 316
no change	Stainless Steel 304

4.7.3 Accelerated Rate Calorimetry. In view of the results seen for Copper NarloyZ and quadricyclane in the hot tube test, we pursued more comprehensive, quantitative data on the apparent instability of hot quadricyclane in the presence of copper. First we must reiterate that quadricyclane is known to revert back to its precursor (norbornadiene) at elevated temperatures in even the most inert materials. Our interest was to identify common materials which might greatly accelerate this reaction and thus pose an unusual hazard to those handling and using quadricyclane propellants.

The ARC testing first established a decomposition rate for quadricyclane in a clean, inert titanium sample holder. The onset was detected at 417 K with a (back) extrapolated rate of decomposition of 8.6×10^{-8} mole s^{-1} at 415 K. Samples in contact with NarloyZ had an average onset temperature of 411 K and an observed rate of 1.5×10^{-7} mole s^{-1} at 415 K. Thus NarloyZ accelerates the decomposition of quadricyclane by 1.8 over inert material and reduces the detectable onset of reaction from 417 K to 411 K. While this finding is scientifically significant, the practical differences between inert materials and copper NarloyZ are insignificant. Quadricyclane will not be suitable for propulsion systems where it is exposed to temperatures above about 400K (~127°C, 261°F) for longer than a few minutes whether it is in contact with copper NarloyZ or inert material such as Stainless Steel 304 or glass.

4.8 Detonation Sensitivity

Quadricyclane is a hydrocarbon molecule and would not normally contain much oxygen. As such, violent explosive combustion reactions characteristic of other propellants such as ammonium perchlorate or RDX cannot occur. However, quadricyclane has a large positive heat of formation like hydrazine or acetylene and could possibly be induced to rapidly decompose or polymerize, releasing large amounts of heat or high pressure gas. Unlike hydrazine or acetylene, quadricyclane is a complex interconnected molecule so that simple fast exothermic reactions leading to low-energy products are less likely. Our interest was to determine what types of reactions may occur if quadricyclane were exposed to the standard detonation-inducing conditions of impact, friction and donor-charge detonation.

In all three cases, quadricyclane recorded a negative response to detonation tests at the most energetic settings (maximum drop weight 2.5 kg x 48 cm, maximum friction of

37.8 kg x 30.0 cm, zero card). In the case of impact, we were able to recover the test material after 2.5 kg drop of 48 cm and determine that the material was unchanged (GC) by the impact. The impact did not induce any type of decomposition or polymerization. Samples from the negative friction and card-gap tests were not recoverable.

A further hazard test was arranged with the NASA-White Sands facility. Adiabatic compression will be tested there and reported separately.

5. CONCLUSIONS AND RECOMMENDATIONS

We have investigated various chemical, physical and hazards properties of quadricyclane and quadricyclane/RP-1 blends. Quadricyclane has $\Delta Hf = +72.2$ kcal/mol[6] versus -5.76 kcal/mol[9] for RP-1 (CH_2 molar unit) and is calculated to be 20% denser than RP-1. Quadricyclane is significantly more volatile than RP-1 which may produce better vaporization and combustion in a rocket engine, but also leads to a much lower flash point (2°C versus 110°C for RP-1) and a greater potential fire hazard. Other physical properties such as viscosity, melting point, boiling point and thermal conductivity also differ from the RP-1 values, but are within common operational limits for propellants. We did see evidence that quadricyclane would begin to slowly decompose at temperatures above about 127°C (261°F), but were able to safely store and handle quadricyclane with a few precautions (blanket with nitrogen gas, exclude light) common to normal propellant operations.

We believe that quadricyclane offers significant performance and density advantages over kerosene-based RP-1 as a rocket propellant. These advantages should be attainable in current RP-1/LOX based hardware since the properties of quadricyclane are not dramatically different from RP-1. A propulsion system specifically designed for quadricyclane/LOX would be able to take full advantage of the higher combustion performance and increased fuel density resulting in a smaller yet more capable vehicle.

REFERENCES

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9. Manufacturers MSDS supplied with commercial materials.

10. Bondi, A. Physical Properties of Molecular Crystals, Liquids, and Glasses, John Wiley & Sons, Inc., New York, 1968.

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APPENDIX A

THERMAL CONDUCTIVITY REPORT

BY

INSTITUTE FOR RESEARCH, INC.

INSTITUTE FOR RESEARCH, INC.
8330 WESTGLEN DR. • HOUSTON, TEXAS 77063 • 713/783-8400 • FAX 713/783-8401

September 26, 1994

A. Wilson
Hughes STX Corporation
c/o Phillips Lab
Building 8451
Edwards AFB, CA 93524

RE: Contract #FO4611-93-C-0005
P.O.# J1962P

ANALYTICAL REPORT

SUBJECT: Determination of Thermal Conductivity (K Factor) of Quadricyclane (99%) at -40°C, -10°C, 20°C, 50°C, 80°C and 100°C.

METHOD: ASTM E-1225, D2717 - Guarded Hot Plate Method

RESULTS:

Temperature, °C	K Factor, cal/(sec)(cm^2)(°C/cm)
-40	0.0003969
-10	0.0003787
20	0.0003515
50	0.0003250
80	0.0003121
100	0.0002844

Respectfully submitted,

Benjamin Mosier

Benjamin Mosier, Ph.D., FAIC
President

BM:dzm

Reference: SW-0926942

APPENDIX B

WSTF 96-29649
8 March 1996

MATERIALS COMPATIBILITY TESTS:
THE VALENCE ISOMERIZATION OF QUADRICYCLANE BY
ACCELERATING RATE CALORIMETRY
SPECIAL TEST REPORT

NASA WHITE SANDS TEST FACILITY

MATERIALS COMPATIBILITY TESTS: THE VALENCE ISOMERIZATION OF QUADRICYCLANE BY ACCELERATING RATE CALORIMETRY SPECIAL TEST DATA REPORT

WSTF # 96-29649
March 8, 1996

1.0 INTRODUCTION

The NASA White Sands Test Facility (WSTF) was requested by Phillips Laboratory/ Hughes STX to investigate thermal hazards associated with quadricyclane (quadricyclo[2.2.1.$0^{2,6}$.$0^{3,5}$]heptane). Quadricyclane is a high-energy, high-density compound which exothermically isomerizes to norbornadiene (bicyclo[2.2.1]hepta-2,5-diene). The high heat of formation of quadricyclane ($\Delta H_{f\,(g)}^{o}$ = 339 kJ mole^{-1}) suggests its use as an additive to liquid hydrocarbon propellants.

The isomerization of quadricyclane to norbornadiene is known to be catalyzed by transition metal compounds. This catalysis raises compatibility issues, particularly with the ferrous- and copper-based alloys used in propellant systems.

WSTF has broad experience in the study of propellant system materials compatibility and thermal hazards based on the technique of accelerating rate calorimetry (ARC). WSTF has published manuals containing the results of hydrazine and monomethylhydrazine ARC studies.[1,2]

2.0 OBJECTIVE

Determine the isomerization rate of quadricyclane using an accelerating rate calorimeter.

---

[1] Pedley, M. D., D. L. Baker, H. D. Beeson, R. C. Wedlich, F. J. Benz, R. L. Bunker, and N. B. Martin. *Fire, Explosion, Compatibility, and Safety Hazards of Hydrazine*. RD-WSTF-0002, February 20, 1990.

[2] Woods, S. S., D. B. Wilson, R. L. Bunker, D. L. Baker, and N. B. Martin. *Fire, Explosion, Compatibility, and Safety Hazards of Monomethylhydrazine*. RD-WSTF-0003, May 5, 1993.

NASA WHITE SANDS TEST FACILITY

MATERIALS COMPATIBILITY TESTS:
THE VALENCE ISOMERIZATION OF QUADRICYCLANE BY ACCELERATING RATE CALORIMETRY
SPECIAL TEST DATA REPORT

WSTF # 96-29649
March 8, 1996

3.0 TEST MATERIAL

Test Material Name:	Quadricyclane
WSTF Material Number:	96-29649
Vendor Name:	Aldrich Chemical Co.
Address:	P.O. Box 14508, St. Louis, MO 63167
Lot Number:	MZ029025JL
Chemical Class:	Organic Compound
Appearance:	Clear Liquid

4.0 TEST DOCUMENT

JSC Form 2035 (Appendix)

5.0 EXPERIMENTAL APPROACH

A commercial accelerating rate calorimeter (Columbia Scientific Industries, Austin, TX) was used to determine the isomerization rate of quadricyclane.

The calorimeter consists of an insulated chamber that surrounds the reaction vessel. The reaction vessel is a 2.54-cm- (1-in.-) diameter sphere made of commercially pure titanium with a volume of 9 mL. The calorimeter is divided into separate zones that are individually temperature controlled using thermocouples, cartridge heaters, and a microprocessor. A thermocouple is also attached to the reaction vessel.

Before use, the reaction vessel was cleaned in a two-step process. First, the vessel was cleaned with detergent and aqueous sodium hydroxide and rinsed with tap water. Next, the vessel was cleaned with a phosphoric acid/2-butoxyethanol solution and rinsed with tap water followed by a deionized water rinse. Finally, the vessel was

dried with gaseous nitrogen. The clean reaction vessel was fitted with a stainless steel 316L ferrule and plug and was weighed at 24 g. The reaction vessel was then purged with nitrogen, charged with 1.0 mL of quadricyclane, sealed with the plug, and reweighed. Next, the reaction vessel was shaken to wet all internal surfaces with quadricyclane, connected to a thermocouple, and suspended in the ARC. The ARC experiment was then initiated. At the completion of the test, the reaction vessel was cooled and reweighed as a check for leaks. Testing was repeated until three reproducible tests were obtained.

6.0 EXPERIMENTAL RESULTS

Time-temperature data for the thermal isomerization of quadricyclane were analyzed using a thermokinetic model developed at WSTF. Log(rate) vs inverse temperature plots of three runs are shown in Figure 1. Activation parameters for use in the Arrhenius equation:

$$k = Ae^{(-Ea/RT)}$$

where k is the first-order rate constant (sec^{-1}) for the isomerization of quadricyclane to norbornadiene, A is the pre-exponential term, Ea is the activation energy ($kJ\ mole^{-1}$), R is the universal gas constant (8.314×10^{-3} $kJ\ mole^{-1}$), and T is the absolute temperature (K) were calculated over the temperature range 417 to 442 K.

The activation parameters for the isomerization reaction are given in Table 1.

Under the standard test conditions used at WSTF, the average onset temperature for the isomerization of quadricyclane with no added metal powder is 417 K. However, the onset temperature is system dependent and does not imply that isomerization always begins at that temperature.

NASA WHITE SANDS TEST FACILITY

MATERIALS COMPATIBILITY TESTS:
THE VALENCE ISOMERIZATION OF QUADRICYCLANE BY ACCELERATING RATE CALORIMETRY
SPECIAL TEST DATA REPORT

WSTF # 96-29649
March 8, 1996

Table 1. Activation Parameters for Quadricyclane Isomerization

Number	A (sec^{-1})	Ea (kJ $mole^{-1}$)
Quad 1799	1.1×10^{15}	160.0
Quad 2040	1.6×10^{16}	169.1
Quad 2045	3.6×10^{15}	164.2
Average	$6.9 \pm 1.3 \times 10^{15}$	164.5 ± 0.9

The average activation parameters were calculated from the mean rate at each temperature as a function of temperature and are presented with estimated standard errors. From the averaged activation parameters, the reaction rate at 415 K was calculated to be 8.6×10^{-8} mole sec^{-1}. Using the value of -91.5 kJ $mole^{-1}$ for the vapor phase heat of isomerization, the heat generation rate was calculated to be -7.8×10^{-6} kJ sec^{-1}.

7.0 TEST SUMMARY

The isomerization rate of quadricyclane was determined using ARC. The Arrhenius activation parameters, A and Ea, were calculated and reported. The rate of isomerization was found to be 8.6×10^{-8} moles sec^{-1} at 415 K.

NASA WHITE SANDS TEST FACILITY

MATERIALS COMPATIBILITY TESTS: THE VALENCE ISOMERIZATION OF QUADRICYCLANE BY ACCELERATING RATE CALORIMETRY SPECIAL TEST DATA REPORT

WSTF # 96-29649
March 8, 1996

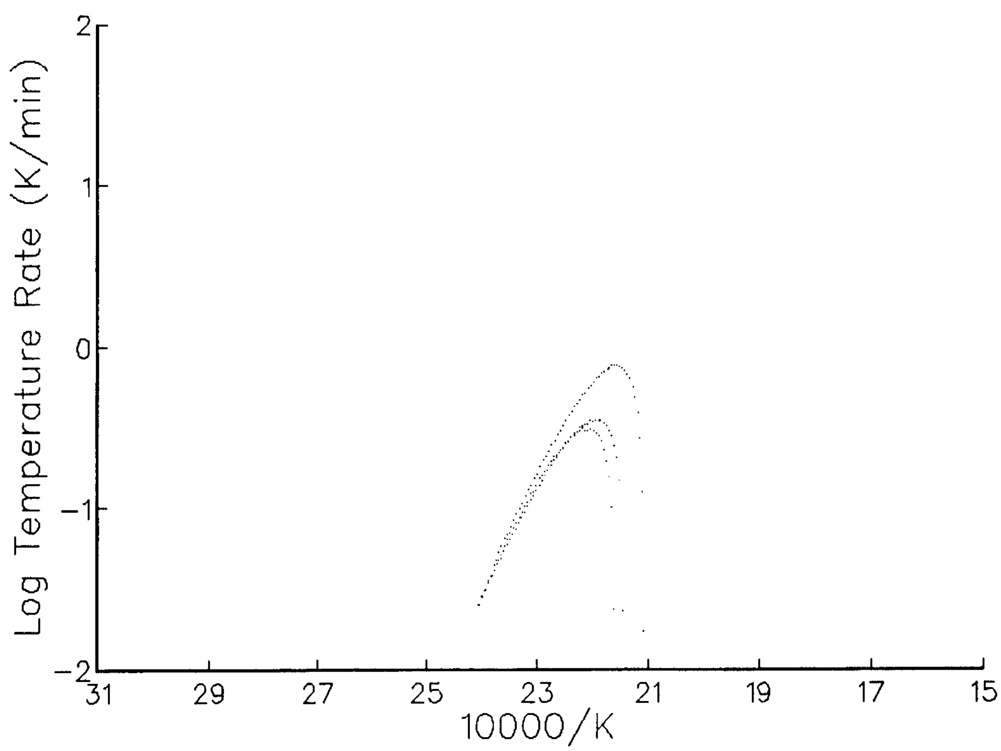

Figure 1. Test Results for Runs Quad1799, Quad2040, and Quad2045

NASA WHITE SANDS TEST FACILITY

MATERIALS COMPATIBILITY TESTS: THE VALENCE ISOMERIZATION OF QUADRICYCLANE BY ACCELERATING RATE CALORIMETRY SPECIAL TEST DATA REPORT

WSTF # 96-29649
March 8, 1996

Prepared by: ______________________
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Approved by: ______________________ 3/19/96
David L. Baker
NASA Laboratories Office

NASA WHITE SANDS TEST FACILITY

MATERIALS COMPATIBILITY TESTS:
THE VALENCE ISOMERIZATION OF QUADRICYCLANE BY ACCELERATING RATE CALORIMETRY
SPECIAL TEST DATA REPORT

WSTF # 96-29649
March 8, 1996

APPENDIX

JSC Form 2035

NASA JSC TEST REQUEST

NOTE TO TEST FACILITY: A COPY OF THIS REQUEST SHOULD BE RETURNED WITH THE TEST REPORT.

OFFICE USE ONLY		
TEST FACILITY I.D. NUMBER 96-29649		
NAME Angelica Wilson/Dave Baker	ORGANIZATION OL-AC PL/RKF NASA/RF	COORDINATOR DB
ADDRESS Phillips Laboratory/Hughes STX 10 E. Saturn Blvd. Edwards AFB, CA 93524	White Sands Test Facility Las Cruces, NM 88004	REQUEST NO. WSTF TEST FACILITY WSTF
DATE January 02, 1996	PHONE (805) 275-5317/(505) 524-5605	CODE

1. MANUFACTURER'S IDENTIFICATION (ITEM DESCRIPTION) Quadricyclane	2. MANUFACTURER'S NAME Aldrich Chemical Co. P.O. Box 14508 St. Louis, MO 63167

3. SPECIFICATION	4. CHEMICAL CLASS	5. GENERIC USE

6. CHECK CATEGORY NHB 8060.1 A, B, C NHB 8060.1C	7. TEST REQUIRED 1 THROUGH 18, VCM, TQCM, SPECIAL Special-Accelerated Rate Calorimetry

8. VEHICLE	9. PART NUMBER/SERIAL NO. Lot MZ029025JL	10. PROJECT ARC Quadricyclane	11. USE TEMPERATURE
12. USE ATMOSPHERE/FLUID	13. IGNITER TYPE	14. USE PRESSURE	15. USE THICKNESS

16. INTENDED APPLICATION	17. QTY IN HABITABLE AREA/HAZARDOUS FLUID/VACUUM

18. CURE TIME	19. CURE TEMPERATURE	20. CURE PRESSURE

21. TEST ARTICLE WT.	22. TEST ARTICLE AREA	23. NUMBER OF ITEMS TESTED	24. NO. OF ITEMS TO BE FLOWN
25. TEST CHAMBER VOLUME	26. TEST CHAMBER ATMOSPHERE	27. TEST CHAMBER PRESSURE	28. TEST CHAMBER TEMPERATURE
29. TEST CHAMBER DURATION	30. CLEANING SPEC	31. MATERIAL CODE	32. PHOTOGRAPHIC COVERAC VIDEO: No STILLS: No

33. SPECIAL INSTRUCTIONS

APPENDIX C

WSTF 96-29649
4 February 1997

QUADRICYCLANE RAPID COMPRESSION TESTING SPECIAL TEST DATA REPORT

NASA WHITE SANDS TEST FACILITY

QUADRICYLANE RAPID COMPRESSION TESTING
SPECIAL TEST DATA REPORT

WSTF # 96-30249
February 4, 1997

1.0 INTRODUCTION

The White Sands Test Facility (WSTF) was requested by Phillips Laboratory to conduct rapid compression (adiabatic compression) tests with quadricyclane (C_7H_8) liquid and a nitrogen gas ullage. The purpose of the tests was to determine if the surge pressure reaction threshold of C_7H_8 liquid is less than 69 MPa (10,000 psia).

Previous testing at WSTF investigated the conditions that initiated explosive decomposition of hydrazine (N_2H_4) liquid by rapid compression of nitrogen gas ullages.[1] Tests were performed in which columns of liquid N_2H_4 were accelerated into dead-headed lines containing nitrogen gas ullages at ambient temperatures. Initiation of explosive decomposition of N_2H_4 was caused by adiabatic heating of the ullage gas which was dependent on the hydrodynamic surge pressure generated when the liquid columns impacted at the dead heads. It was determined that a surge pressure of 17 MPa (2500 psia) was required to initiate rapid N_2H_4 decomposition.

The current testing subjected C_7H_8 to four times the threshold surge pressure at which N_2H_4 rapidly decomposes.

2.0 TEST DOCUMENT

JSC Form 2035 (Appendix)

3.0 APPROACH

To provide a comparison with a known fluid, water and C_7H_8 were tested in the same test article configuration used in previous testing.

The test articles consisted of two parts (Figure 1). The first part was a 20–cm

[1] Baker, D., H. Beeson, D. Fernandez. M. Plaster. and F. Benz. "Explosive Decomposition of Hydrazine by Rapid Compression of Gas Ullages." Paper presented at the *JANNAF Safety and Environmental Protection Subcommittee Meeting*, Monterey, CA, May 23-27, 1988.

(8–in.) long by 1.27–cm (0.5–in.) diameter piece of stainless steel tubing filled with the test fluid. The second part was a 38–cm (15–in.) long by 1.27–cm (0.5–in.) diameter piece of stainless steel tubing filled with the ullage gas or vapor. The two parts were joined by a fitting but were separated by a 5–mil-thick Teflon® diaphragm. A high-speed, piezoelectric pressure transducer was mounted in a stainless steel plug that served as a dead-head to measure surge pressures. A thermocouple located in the liquid column provided pretest liquid temperature data.

Once filled and assembled, the test articles were installed in the test system. The test system consisted of a nitrogen source, a helium source, an accumulator, and a pneumatically actuated high-speed ball valve. When actuated with helium gas, the ball valve opened within approximately 8 ms. Nitrogen gas was used to pressurize the accumulator and to purge the test article interface during installation. To complete the installation, the bottom half of the test article was purged with nitrogen for 1 min and then allowed to vent to ambient pressure before the plug fitting was tightened.

Once installation of the test article was complete, the accumulator was pressurized to the desired driver pressure. Initial testing was performed with water to determine the driver pressure required to achieve a 69 MPa (10,000 psia) surge pressure.

4.0 RESULTS AND DISCUSSION

Test results are shown in Table 1. The data are archived on video cassette number WSTF # 996-0636-A.

Based on the water test results, it was determined that a driver pressure of 2.4 MPa (350 psia) was required to produce a 69 MPa (10,000 psia) surge pressure to run the C_7H_8 tests. There was no visible evidence of reactions from any of the three trials. The measured surge pressures were consistent with the water results. During test 30, the data acquisition system triggered late and missed the event; therefore, no pressure data are recorded for that test. However, the pre- and posttest conditions from test 30 were the same as tests 31 and 32, which indicates it may have attained a surge pressure of approximately 69 MPa (10,000 psia) and that the C_7H_8 did not react.

NASA WHITE SANDS TEST FACILITY

QUADRICYLANE RAPID COMPRESSION TESTING
SPECIAL TEST DATA REPORT

WSTF # 96-30249
February 4, 1997

5.0 SUMMARY

It has been previously determined that a surge pressure of 17 MPa (2500 psia) is required to initiate rapid N_2H_4 decomposition.[1]

Based on a comparison with the water test results, C_7H_8 did not react when subjected to surge pressures of 69 MPa (10,000 psia).

[1] Baker, D., H. Beeson, D., Fernandez, M. Plaster, and F. Benz. "Explosive Decomposition of Hydrazine by Rapid Compression of Gas Ullages." Paper presented at the *JANNAF Safety and Environmental Protection Subcommittee Meeting,* Monterey, CA, May 23-27, 1988.

NASA WHITE SANDS TEST FACILITY

QUADRICYLANE RAPID COMPRESSION TESTING
SPECIAL TEST DATA REPORT

WSTF # 96-30249
February 4, 1997

Table 1
Test Results with Gaseous Nitrogen

Test No.	Fluid	Valve Speed (ms)	Fluid Temp (°C)	Pressure Ullage (psia)	Pressure Driver (psia)	Pressure Transducer (psia)
1	H_2O	8.4	20	12.3	101.6	516.0
2	H_2O	8.2	24	12.3	102.5	600.0
3	H_2O	8.3	22	12.3	100.0	933.7
4	H_2O	8.4	19	12.2	100.8	609.1
5	H_2O	8.1	20	12.2	101.8	591.1
6	H_2O	8.0	21	12.2	302.0	8632.7
7	H_2O	8.3	22	12.2	300.9	8454.5
8	H_2O	8.2	22	12.2	302.4	8778.6
9	H_2O	8.0	18	12.2	202.3	3690.9
10	H_2O	8.4	18	12.2	200.7	3734.4
11	H_2O	8.3	18	12.2	201.2	4043.6
12	H_2O	8.2	18	12.2	150.6	1622.1
13	H_2O	8.1	18	12.2	151.0	1818.8
14	H_2O	8.4	18	12.2	150.6	1798.6
15	H_2O	8.2	20	12.2	250.0	6500.1
16	H_2O	8.2	19	12.2	251.0	6248.7
17	H_2O	8.2	19	12.2	250.3	6337.0
18	H_2O	8.0	19	12.2	251.1	5954.9
19	H_2O	8.1	19	12.2	350.8	10075
20	H_2O	8.0	19	12.2	350.3	10075
21	H_2O	8.4	17	12.4	350.3	9888.8
22	H_2O	8.3	18	12.4	351.4	10280.5
23	H_2O	8.2	18	12.4	352.4	10180.4
24	H_2O	8.9	16	12.3	125.7	894.2
25	H_2O	8.1	16	12.3	125.5	997.1
26	H_2O	8.1	16	12.3	125.4	845.0

NR = Not Recorded. Data acquisition system triggered late and missed event.

NASA WHITE SANDS TEST FACILITY

QUADRICYLANE RAPID COMPRESSION TESTING
SPECIAL TEST DATA REPORT

WSTF # 96-30249
February 4, 1997

Table 1
Test Results with Gaseous Nitrogen (Continued)

Test No.	Fluid	Valve Speed (ms)	Fluid Temp (°C)	Pressure Ullage (psia)	Pressure Driver (psia)	Pressure Transducer (psia)
27	H_2O	8.1	16	12.3	174.0	2470.9
28	H_2O	7.9	16	12.3	175.4	2555.4
29	H_2O	7.9	17	12.3	174.5	3292.1
30	C_7H_8	NR	22	12.3	NR	NR
31	C_7H_8	8.0	22	12.3	352.6	9954.0
32	C_7H_8	7.9	22	12.3	350.4	10133.6

NR = Not Recorded. Data acquisition system triggered late and missed event.

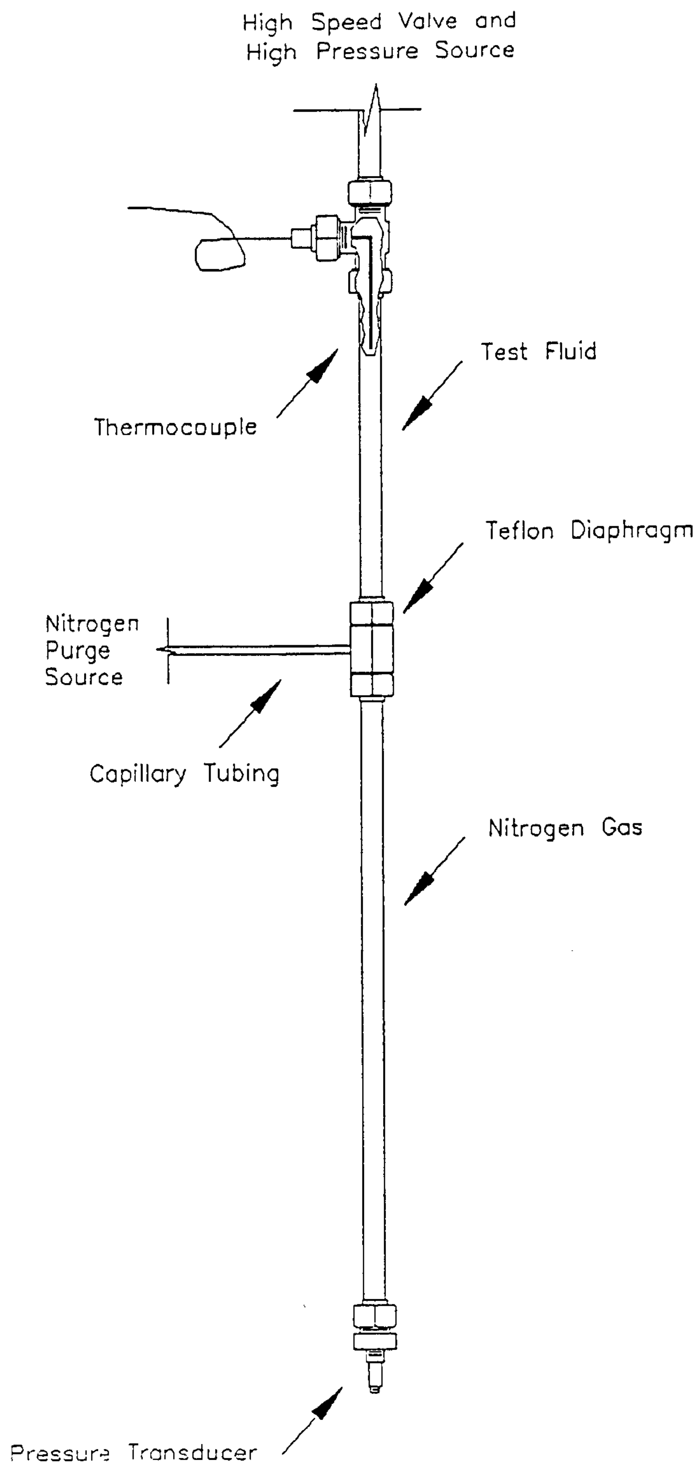

Figure 1
Test Article

NASA WHITE SANDS TEST FACILITY

QUADRICYLANE RAPID COMPRESSION TESTING
SPECIAL TEST DATA REPORT

WSTF # 96-30249
February 4, 1997

Prepared by: Kurt Rathgeber
Kurt Rathgeber
AlliedSignal Technical Services Corp. Team

Reviewed by: Larry Bamford
Larry Bamford
AlliedSignal Technical Services Corp. Team

Approved by: David Baker
David Baker
NASA Laboratories Office

NASA WHITE SANDS TEST FACILITY

QUADRICYLANE RAPID COMPRESSION TESTING
SPECIAL TEST DATA REPORT

WSTF # 96-30249
February 4, 1997

APPENDIX

JSC Form 2035

NASA JSC TEST REQUEST

NOTE TO TEST FACILITY: A COPY OF THIS REQUEST SHOULD BE RETURNED WITH THE TEST REPORT.

NAME Angelica Cabrera	ORGANIZATION Hughes STX	OFFICE USE ONLY TEST FACILITY I.D. NUMBER 96-30249 COORDINATOR DB
ADDRESS OL-AC PL/RKF 10 E. Saturn Blvd. Edwards AFB, CA 93524-7680		REQUEST NO. WSTF TEST FACILITY WSTF
DATE September 03, 1996	PHONE (805) 275-5317	CODE

1. MANUFACTURER'S IDENTIFICATION (ITEM DESCRIPTION) Quadricyclane	2. MANUFACTURER'S NAME	
3. SPECIFICATION	4. CHEMICAL CLASS Hydrocarbon	5. GENERIC USE
6. CHECK CATEGORY NHB 8060.1 A, B, C NHB 8060.1C	7. TEST REQUIRED 1 THROUGH 18, VCM, TQCM, SPECIAL Special	

8. VEHICLE	9. PART NUMBER/SERIAL NO.	10. PROJECT FBQ	11. USE TEMPERATURE
12. USE ATMOSPHERE/FLUID	13. IGNITER TYPE	14. USE PRESSURE	15. USE THICKNESS
16. INTENDED APPLICATION		17. QTY IN HABITABLE AREA/HAZARDOUS FLUID/VACUUM	
18. CURE TIME	19. CURE TEMPERATURE	20. CURE PRESSURE	
21. TEST ARTICLE WT.	22. TEST ARTICLE AREA	23. NUMBER OF ITEMS TESTED	24. NO. OF ITEMS TO BE FLOWN
25. TEST CHAMBER VOLUME	26. TEST CHAMBER ATMOSPHERE	27. TEST CHAMBER PRESSURE	28. TEST CHAMBER TEMPERATURE
29. TEST CHAMBER DURATION	30. CLEANING SPEC	31. MATERIAL CODE	32. PHOTOGRAPHIC COVERAGE VIDEO: No STILLS: No

33. SPECIAL INSTRUCTIONS

Subject quadricyclane (C_7H_8) liquid to surge pressures on the order of 10,000 psig to determine if it will undergo an explosive event due to rapid compression of a gas ullage.

JSC FORM 2035

National Aeronautics and
Space Administration

Lyndon B. Johnson Space Center
White Sands Test Facility
P.O. Box 20
Las Cruces, NM 88004-0020

Reply to Attn of: RF

Hughes STX
Attn: Angelica Cabrera/OL-AC PL/RKF
10 E. Saturn Blvd.
Edwards AFB, CA 93524-7680

Subject: Materials Test Data Transmittal

Enclosed are the results of tests recently performed at the NASA White Sands Test Facility laboratories.

Please direct any questions that may arise from this data transmittal to Dave Baker at 505-524-5605.

Harry T. Johnson

Harry T. Johnson
Chief, Laboratories

Enclosure

APPENDIX D

WSTF 96-29650
8 March 1996

MATERIALS COMPATIBILITY TESTS: EFFECTS OF STAINLESS STEEL 304L ON THE VALENCE ISOMERIZATION OF QUADRICYCLANE BY ACCELERATING RATE CALORIMETRY SPECIAL TEST DATA REPORT

NASA WHITE SANDS TEST FACILITY

MATERIALS COMPATIBILITY TESTS: EFFECTS OF STAINLESS STEEL 304L ON THE VALENCE ISOMERIZATION OF QUADRICYCLANE BY ACCELERATING RATE CALORIMETRY SPECIAL TEST DATA REPORT

WSTF # 96-29650
March 8, 1996

1.0 INTRODUCTION

The NASA White Sands Test Facility (WSTF) was requested by Phillips Laboratory/ Hughes STX to investigate thermal hazards associated with quadricyclane (quadricyclo[2.2.1.$0^{2,6}$.$0^{3,5}$]heptane). Quadricyclane is a high-energy, high-density compound which exothermically isomerizes to norbornadiene (bicyclo[2.2.1]hepta-2,5-diene). The high heat of formation of quadricyclane ($\Delta H_{f}^{o}{}_{(g)}$ = 339 kJ mole^{-1}) suggests its use as an additive to liquid hydrocarbon propellants.

The isomerization of quadricyclane to norbornadiene is known to be catalyzed by transition metal compounds. This catalysis raises compatibility issues, particularly with the ferrous- and copper-based alloys used in propellant systems.

WSTF has broad experience in the study of propellant system materials compatibility and thermal hazards based on the technique of accelerating rate calorimetry (ARC). WSTF has published manuals containing the results of hydrazine and monomethylhydrazine ARC studies.[1,2]

2.0 OBJECTIVE

Determine the effect of Stainless Steel 304L (SS304L) powder on the isomerization rate of quadricyclane using an accelerating rate calorimeter.

---

1 Pedley, M. D., D. L. Baker, H. D. Beeson, R. C. Wedlich, F. J. Benz, R. L. Bunker, and N. B. Martin. *Fire, Explosion, Compatibility, and Safety Hazards of Hydrazine*. RD-WSTF-0002, February 20, 1990.

2 Woods, S. S., D. B. Wilson, R. L. Bunker, D. L. Baker, and N. B. Martin. *Fire, Explosion, Compatibility, and Safety Hazards of Monomethylhydrazine*. RD-WSTF-0003, May 5, 1993.

NASA WHITE SANDS TEST FACILITY

MATERIALS COMPATIBILITY TESTS:
EFFECTS OF STAINLESS STEEL 304L ON THE VALENCE ISOMERIZATION OF QUADRICYCLANE BY ACCELERATING RATE CALORIMETRY
SPECIAL TEST DATA REPORT

WSTF # 96-29650
March 8, 1996

3.0 TEST MATERIALS

Material Name:	Stainless Steel 304L
Material Number:	96-29650
Vendor Name:	Alfa Products
Address:	152 Andover St., Danvers, MA 01923
Lot Number:	010484
Chemical Class:	Alloy
Specific Surface Area:	0.192 m^2 g^{-1}
Appearance:	Grey Powder

Test Material Name:	Quadricyclane
WSTF Material Number:	96-29649
Vendor Name:	Aldrich Chemical Co.
Address:	P.O. Box 14508, St. Louis, MO 63167
Lot Number:	MZ029025JL
Chemical Class:	Organic Compound
Appearance:	Clear liquid

4.0 TEST DOCUMENT

JSC Form 2035 (Appendix)

5.0 EXPERIMENTAL APPROACH

A commercial accelerating rate calorimeter (Columbia Scientific Industries, Austin, TX) was used to determine the isomerization rate of quadricyclane.

NASA WHITE SANDS TEST FACILITY

MATERIALS COMPATIBILITY TESTS: EFFECTS OF STAINLESS STEEL 304L ON THE VALENCE ISOMERIZATION OF QUADRICYCLANE BY ACCELERATING RATE CALORIMETRY SPECIAL TEST DATA REPORT

WSTF # 96-29650
March 8, 1996

The calorimeter consists of an insulated chamber that surrounds the reaction vessel. The reaction vessel is a 2.54-cm- (1-in.-) diameter sphere made of commercially pure titanium with a volume of 9 mL. The calorimeter is divided into separate zones that are individually temperature controlled using thermocouples, cartridge heaters, and a microprocessor. A thermocouple is also attached to the reaction vessel.

Before use, the reaction vessel was cleaned in a two-step process. First, the vessel was cleaned with detergent and aqueous sodium hydroxide and rinsed with tap water. Next, the vessel was cleaned with a phosphoric acid/2-butoxyethanol solution and rinsed with tap water followed by a deionized water rinse. Finally, the vessel was dried with gaseous nitrogen. The clean reaction vessel was fitted with a stainless steel 316L ferrule and plug and was weighed at 24 g. The reaction vessel was then loaded with 0.5 g of metal sample, purged with nitrogen, charged with 1.0 mL of quadricyclane, sealed with the plug, and reweighed. Next, the reaction vessel was shaken to wet all internal surfaces with quadricyclane, connected to a thermocouple, and suspended in the ARC. The ARC experiment was then initiated. At the completion of the test, the reaction vessel was cooled and reweighed as a check for leaks. Testing was repeated until three reproducible tests were obtained.

The surface area of the SS304L powder was determined using a Flowsorb II 2300 (Micromeritics) with a gas mixture of 21.8 percent nitogen in helium. The SS304L powder had a specific area of 0.192 m^2 $g^{-1.}$ The surface area of a reference powder was measured immediately before that of the sample.

6.0 EXPERIMENTAL RESULTS

Time-temperature data for the thermal isomerization of quadricyclane in the presence of SS304L powder were analyzed using a thermokinetic model developed at WSTF. Log(rate) vs inverse temperature plots of three runs are shown in Figure 1.

NASA WHITE SANDS TEST FACILITY

MATERIALS COMPATIBILITY TESTS: EFFECTS OF STAINLESS STEEL 304L ON THE VALENCE ISOMERIZATION OF QUADRICYCLANE BY ACCELERATING RATE CALORIMETRY SPECIAL TEST DATA REPORT

WSTF # 96-29650
March 8, 1996

Activation parameters for use in the Arrhenius equation:

$$k = Ae^{(-Ea/RT)}$$

where k is the first-order rate constant (sec^{-1}) for the isomerization of quadricyclane to norbornadiene, A is the pre-exponential term, Ea is the activation energy (kJ $mole^{-1}$), R is the universal gas constant (8.314×10^{-3} kJ $mole^{-1}$), and T is the absolute temperature (K) were calculated over the temperature range 414 to 469 K.

The activation parameters for the isomerization reactions are given in Table 1.

Under the standard test conditions used at WSTF, the average onset temperature for the isomerization of quadricyclane with no added metal powder is 417 K. However, the onset temperature is system dependent and does not imply that isomerization always begins at that temperature. Using WSTF test conditions, the average onset temperature in the presence of SS304L was 414 K.

Table 1. Activation Parameters for Quadricyclane Isomerization with SS304L

Number	A (sec^{-1})	Ea (kJ $mole^{-1}$)
Quad 1802	1.4×10^{14}	151.3
Quad 2046	1.7×10^{15}	160.4
Quad 2049	1.5×10^{15}	159.7
Average	$1.1 \pm 0.2 \times 10^{15}$	157.1 ± 0.6

The average activation parameters were calculated from the mean rate at each temperature as a function of temperature and are presented with estimated standard errors. From the averaged activation parameters, the reaction rate at 415 K was calculated to be 1.3×10^{-7} mole sec^{-1}. Using the value of -91.5 kJ $mole^{-1}$ for the vapor phase heat of isomerization, the heat generation rate was calculated to be -1.2×10^{-5} kJ sec^{-1}. The rate at 415 K in the absence of added SS304L metal powder is 8.6×10^{-8} mole sec^{-1}. The isomerization is 1.6 times faster in the presence of SS304L relative to the reaction rate in the absence of SS304L.

7.0 TEST SUMMARY

The effect of SS304L on the isomerization rate of quadricyclane was determined using ARC. The Arrhenius activation parameters, A and Ea, were calculated and reported. The rate of isomerization was found to be 1.3×10^{-7} moles sec^{-1} at 415 K which is 1.6 times that of the isomerization in the absence of 0.1 m^2 of SS304L.

NASA WHITE SANDS TEST FACILITY

MATERIALS COMPATIBILITY TESTS: EFFECTS OF STAINLESS STEEL 304L ON THE VALENCE ISOMERIZATION OF QUADRICYCLANE BY ACCELERATING RATE CALORIMETRY SPECIAL TEST DATA REPORT

WSTF # 96-29650
March 8, 1996

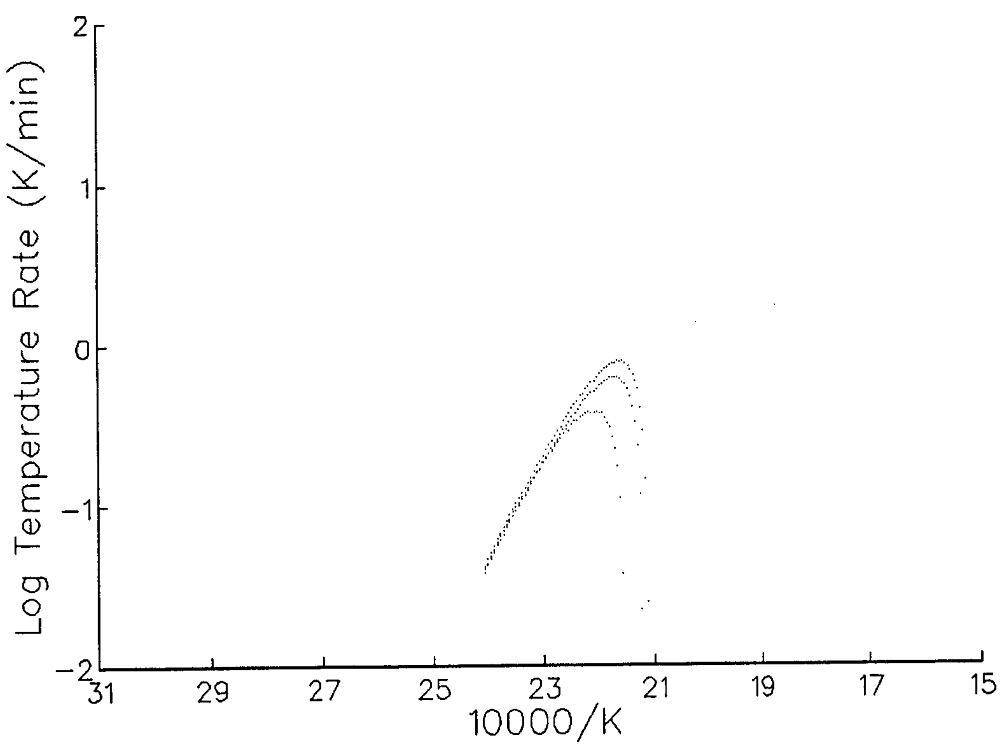

Figure 1. Test Results for Runs Quad1802, Quad2046, and Quad2049

NASA WHITE SANDS TEST FACILITY

MATERIALS COMPATIBILITY TESTS: EFFECTS OF STAINLESS STEEL 304L ON THE VALENCE ISOMERIZATION OF QUADRICYCLANE BY ACCELERATING RATE CALORIMETRY SPECIAL TEST DATA REPORT

WSTF # 96-29650
March 8, 1996

Prepared by: Tom P. Martinez
AlliedSignal Technical Services Corp. Team

Reviewed by: Dennis D. Davis
AlliedSignal Technical Services Corp. Team

Approved by: David L. Baker 3/19/96
NASA Laboratories Office

NASA WHITE SANDS TEST FACILITY

MATERIALS COMPATIBILITY TESTS:
EFFECTS OF STAINLESS STEEL 304L ON THE VALENCE ISOMERIZATION OF QUADRICYCLANE BY ACCELERATING RATE CALORIMETRY
SPECIAL TEST DATA REPORT

WSTF # 96-29650
March 8, 1996

APPENDIX

JSC Form 2035

NASA JSC TEST REQUEST

NOTE TO TEST FACILITY: A COPY OF THIS REQUEST SHOULD BE RETURNED WITH THE TEST REPORT.

OFFICE USE ONLY	
TEST FACILITY I.D. NUMBER	96-29650
COORDINATOR	DB
REQUEST NO.	WSTF
TEST FACILITY	WSTF
CODE	

NAME	Angelica Wilson/Dave Baker
ORGANIZATION	OL-AC PL/RKF NASA/RF
ADDRESS	Phillips Laboratory/Hughes STX 10 E. Saturn Blvd. Edwards AFB, CA 93524 White Sands Test Facility Las Cruces, NM 88004
DATE	January 02, 1996
PHONE	(805) 275-5317/(505) 524-5605
1. MANUFACTURER'S IDENTIFICATION (ITEM DESCRIPTION)	304L Stainless Steel w/Quadricyclane
2. MANUFACTURER'S NAME	Alfa Products 152 Andover St. Danvers, MA 01923 Aldrich Chemical Co. P.O. Box 14508 St. Louis, MO 63167
3. SPECIFICATION	
4. CHEMICAL CLASS	
5. GENERIC USE	
6. CHECK CATEGORY NHB 8060.1 A, B, C	NHB 8060.1C
7. TEST REQUIRED 1 THROUGH 18, VCM, TQCM, SPECIAL	Special-Accelerated Rate Calorimetry
8. VEHICLE	
9. PART NUMBER/SERIAL NO.	Lot 010484
10. PROJECT	ARC Quadricyclane
11. USE TEMPERATURE	
12. USE ATMOSPHERE/FLUID	
13. IGNITER TYPE	
14. USE PRESSURE	
15. USE THICKNESS	
16. INTENDED APPLICATION	
17. QTY IN HABITABLE AREA/HAZARDOUS FLUID/VACUUM	
18. CURE TIME	
19. CURE TEMPERATURE	
20. CURE PRESSURE	
21. TEST ARTICLE WT.	
22. TEST ARTICLE AREA	
23. NUMBER OF ITEMS TESTED	
24. NO. OF ITEMS TO BE FLOWN	
25. TEST CHAMBER VOLUME	
26. TEST CHAMBER ATMOSPHERE	
27. TEST CHAMBER PRESSURE	
28. TEST CHAMBER TEMPERATURE	
29. TEST CHAMBER DURATION	
30. CLEANING SPEC	
31. MATERIAL CODE	
32. PHOTOGRAPHIC COVERA[GE]	VIDEO: No STILLS: No

33. SPECIAL INSTRUCTIONS

The quardricyclane was obtained from WSTF No. 96-29649.

JSC FORM 2035

APPENDIX E

WSTF 96-29651
8 March 1996

MATERIALS COMPATIBILITY TESTS:
EFFECTS OF NICKEL ON THE VALENCE ISOMERIZATION OF QUADRICYCLANE BY ACCELERATING RATE CALORIMETRY
SPECIAL TEST DATA REPORT

NASA WHITE SANDS TEST FACILITY

MATERIALS COMPATIBILITY TESTS: EFFECTS OF NICKEL ON THE VALENCE ISOMERIZATION OF QUADRICYCLANE BY ACCELERATING RATE CALORIMETRY SPECIAL TEST DATA REPORT

WSTF # 96-29651
March 8, 1996

1.0 INTRODUCTION

The NASA White Sands Test Facility (WSTF) was requested by Phillips Laboratory/ Hughes STX to investigate thermal hazards associated with quadricyclane (quadricyclo[2.2.1.$0^{2,6}$.$0^{3,5}$]heptane). Quadricyclane is a high energy, high density compound which exothermically isomerizes to norbornadiene (bicyclo[2.2.1]hepta-2,5-diene). The high heat of formation of quadricyclane ($\Delta H_{f\ (g)}^{o}$ = 339 kJ mole^{-1}) suggests its use as an additive to liquid hydrocarbon propellants.

The isomerization of quadricyclane to norbornadiene is known to be catalyzed by transition metal compounds. This catalysis raises compatibility issues, particularly with the ferrous- and copper-based alloys used in propellant systems.

WSTF has broad experience in the study of propellant system materials compatibility and thermal hazards based on the technique of accelerating rate calorimetry (ARC). WSTF has published manuals containing the results of hydrazine and monomethylhydrazine ARC studies.[1,2]

2.0 OBJECTIVE

Determine the effect of nickel powder on the isomerization rate of quadricyclane using an accelerating rate calorimeter.

---

[1] Pedley, M. D., D. L. Baker, H. D. Beeson, R. C. Wedlich, F. J. Benz, R. L. Bunker, and N. B. Martin. *Fire, Explosion, Compatibility, and Safety Hazards of Hydrazine*. RD-WSTF-0002, February 20, 1990.

[2] Woods, S. S., D. B. Wilson, R. L. Bunker, D. L. Baker, and N. B. Martin. *Fire, Explosion, Compatibility, and Safety Hazards of Monomethylhydrazine*. RD-WSTF-0003, May 5, 1993.

NASA WHITE SANDS TEST FACILITY

MATERIALS COMPATIBILITY TESTS: EFFECTS OF NICKEL ON THE VALENCE ISOMERIZATION OF QUADRICYCLANE BY ACCELERATING RATE CALORIMETRY SPECIAL TEST DATA REPORT

WSTF # 96-29651
March 8, 1996

3.0 TEST MATERIALS

Test Material Name:	Nickel powder
WSTF Material Number:	92-25979
Vendor Name:	Aesar
Address:	P.O. Box 8247, Ward Hill, MA 01835
Lot Number:	J04A03
Chemical Class:	Element
Specific Surface Area:	0.784 m^2 g^{-1}
Appearance:	Grey powder

Test Material Name:	Quadricyclane
WSTF Material Number:	96-29649
Vendor Name:	Aldrich Chemical Co.
Address:	P.O. Box 14508, St. Louis, MO 63167
Lot Number:	MZ029025JL
Chemical Class:	Organic Compound
Appearance:	Clear liquid

4.0 TEST DOCUMENT

JSC Form 2035 (Appendix)

5.0 EXPERIMENTAL APPROACH

A commercial accelerating rate calorimeter (Columbia Scientific Industries, Austin, TX) was used to determine the isomerization rate of quadricyclane.

The calorimeter consists of an insulated chamber that surrounds the reaction vessel.

The reaction vessel is a 2.54-cm- (1-in.-) diameter sphere made of commercially pure titanium with a volume of 9 mL. The calorimeter is divided into separate zones that are individually temperature controlled using thermocouples, cartridge heaters, and a microprocessor. A thermocouple is also attached to the reaction vessel.

Before use, the reaction vessel was cleaned in a two-step process. First, the vessel was cleaned with detergent and aqueous sodium hydroxide and rinsed with tap water. Next, the vessel was cleaned with a phosphoric acid/2-butoxyethanol solution and rinsed with tap water followed by a deionized water rinse. Finally, the vessel was dried with gaseous nitrogen. The clean reaction vessel was fitted with a stainless steel 316L ferrule and plug and was weighed at 24 g. The reaction vessel was then loaded with 0.5 g of metal sample, purged with nitrogen, charged with 1.0 mL of quadricyclane, sealed with the plug, and reweighed. Next, the reaction vessel was shaken to wet all internal surfaces with quadricyclane, connected to a thermocouple, and suspended in the ARC. The ARC experiment was then initiated. At the completion of the test, the reaction vessel was cooled and reweighed as a check for leaks. Testing was repeated until three reproducible tests were obtained.

The surface area of the nickel powder was determined using a Flowsorb II 2300 (Micromeritics) with a gas mixture of 21.8 percent nitrogen in helium. The nickel powder had a specific surface area of 0.784 m^2 g^{-1}. The surface area of a reference powder was measured immediately before that of the sample.

6.0 EXPERIMENTAL RESULTS

Time-temperature data for the thermal isomerization of quadricyclane in the presence of nickel powder were analyzed using a thermokinetic model developed at WSTF. Log(rate) vs inverse temperature plots of three runs are shown in Figure 1.

NASA WHITE SANDS TEST FACILITY

MATERIALS COMPATIBILITY TESTS: EFFECTS OF NICKEL ON THE VALENCE ISOMERIZATION OF QUADRICYCLANE BY ACCELERATING RATE CALORIMETRY SPECIAL TEST DATA REPORT

WSTF # 96-29651
March 8, 1996

Activation parameters for use in the Arrhenius equation:

$$k = Ae^{(-Ea/RT)}$$

where k is the first-order rate constant (sec^{-1}) for the isomerization of quadricyclane to norbornadiene, A is the pre-exponential term, Ea is the activation energy (kJ $mole^{-1}$), R is the universal gas constant (8.314×10^{-3} kJ $mole^{-1}$), and T is the absolute temperature (K) were calculated over the temperature range 410 to 436 K.

The activation parameters for the isomerization reactions are given in Table 1.

Under the standard test conditions used at WSTF, the average onset temperature for the isomerization of quadricyclane with no added metal powder is 417 K. However, the onset temperature is system dependent and does not imply that isomerization always begins at that temperature. Using WSTF test conditions, the average onset temperature in the presence of nickel powder was 410 K.

Table 1. Activation Parameters for Quadricyclane Isomerization with Nickel Powder

Number	A (sec^{-1})	Ea (kJ $mole^{-1}$)
Quad 2056	1.3×10^{15}	158.3
Quad 2058	1.2×10^{15}	158.1
Quad 2061	1.6×10^{15}	159.1
Average	$1.4 \pm 0.3 \times 10^{15}$	158.5 ± 0.7

The average activation parameters were calculated from the mean rate at each temperature as a function of temperature and are presented with estimated standard errors. From the averaged activation parameters, the reaction rate at 415 K was calculated to be 1.7 x 10^{-7} mole sec^{-1}. Using a value of -91.5 kJ $mole^{-1}$ for the vapor phase heat of isomerization, the heat generation rate is calculated to be -1.5 x 10^{-5} kJ sec^{-1}. The rate at 415 K in the absence of added nickel metal powder is 8.6 x 10^{-8} mole sec^{-1}. The isomerization is a factor of 2.0 times faster in the presence of nickel powder relative to the reaction rate in the absence of nickel powder.

7.0 TEST SUMMARY

The effect of nickel on the isomerization rate of quadricyclane was determined using ARC. The Arrhenius activation parameters, A and Ea, were calculated and reported. The rate of isomerization was found to be 1.7 x 10^{-7} moles sec^{-1} at 415 K which is 2.0 times that of the isomerization in the absence of 0.4 m^2 of nickel powder.

NASA WHITE SANDS TEST FACILITY

MATERIALS COMPATIBILITY TESTS: EFFECTS OF NICKEL ON THE VALENCE ISOMERIZATION OF QUADRICYCLANE BY ACCELERATING RATE CALORIMETRY SPECIAL TEST DATA REPORT

WSTF # 96-29651
March 8, 1996

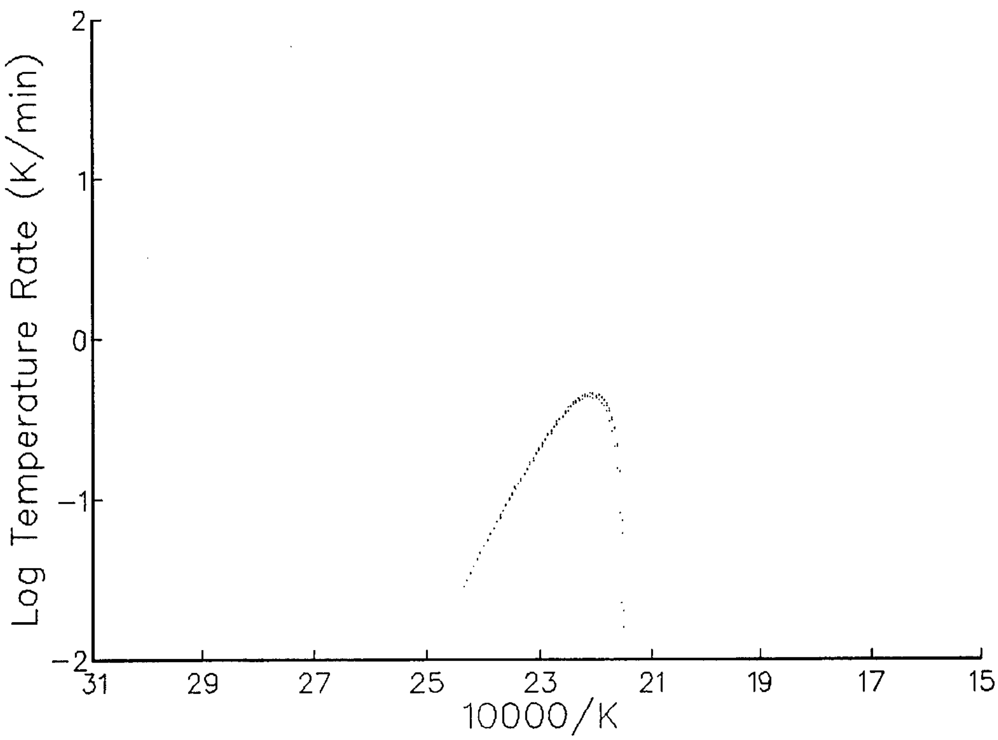

Figure 1. Test Results for Runs Quad2056, Quad2058, and Quad2061

NASA WHITE SANDS TEST FACILITY

MATERIALS COMPATIBILITY TESTS: EFFECTS OF NICKEL ON THE VALENCE ISOMERIZATION OF QUADRICYCLANE BY ACCELERATING RATE CALORIMETRY SPECIAL TEST DATA REPORT

WSTF # 96-29651
March 8, 1996

Prepared by:
Tom P. Martinez
AlliedSignal Technical Services Corp. Team

Reviewed by:
Dennis D. Davis
AlliedSignal Technical Services Corp. Team

Approved by: 3/19/96
David L. Baker
NASA Laboratories Office

NASA WHITE SANDS TEST FACILITY

MATERIALS COMPATIBILITY TESTS:
EFFECTS OF NICKEL ON THE VALENCE ISOMERIZATION OF QUADRICYCLANE BY ACCELERATING RATE CALORIMETRY
SPECIAL TEST DATA REPORT

WSTF # 96-29651
March 8, 1996

APPENDIX

JSC Form 2035

NASA JSC TEST REQUEST

NOTE TO TEST FACILITY: A COPY OF THIS REQUEST SHOULD BE RETURNED WITH THE TEST REPORT.

OFFICE USE ONLY		
TEST FACILITY I.D. NUMBER 96-29651		
NAME Angelica Wilson/Dave Baker	ORGANIZATION OL-AC PL/RKF NASA/RF	COORDINATOR DB
ADDRESS Phillips Laboratory/Hughes STX 10 E. Saturn Blvd. Edwards AFB, CA 93524	White Sands Test Facility Las Cruces, NM 88004	REQUEST NO. WSTF TEST FACILITY WSTF
DATE January 02, 1996	PHONE (805) 275-5317/(505) 524-5605	CODE

1. MANUFACTURER'S IDENTIFICATION (ITEM DESCRIPTION) Nickel w/Quadricyclane	2. MANUFACTURER'S NAME Aldrich Chemical Co. P.O. Box 14508 St. Louis, MO 63167

3. SPECIFICATION	4. CHEMICAL CLASS	5. GENERIC USE

6. CHECK CATEGORY NHB 8060.1 A, B, C NHB 8060.1C	7. TEST REQUIRED 1 THROUGH 18, VCM, TQCM, SPECIAL Special-Accelerated Rate Calorimetry

8. VEHICLE	9. PART NUMBER/SERIAL NO.	10. PROJECT ARC Quadricyclane	11. USE TEMPERATURE
12. USE ATMOSPHERE/FLUID	13. IGNITER TYPE	14. USE PRESSURE	15. USE THICKNESS

16. INTENDED APPLICATION	17. QTY IN HABITABLE AREA/HAZARDOUS FLUID/VACUUM

18. CURE TIME	19. CURE TEMPERATURE	20. CURE PRESSURE

21. TEST ARTICLE WT.	22. TEST ARTICLE AREA	23. NUMBER OF ITEMS TESTED	24. NO. OF ITEMS TO BE FLOWN
25. TEST CHAMBER VOLUME	26. TEST CHAMBER ATMOSPHERE	27. TEST CHAMBER PRESSURE	28. TEST CHAMBER TEMPERATURE
29. TEST CHAMBER DURATION	30. CLEANING SPEC	31. MATERIAL CODE	32. PHOTOGRAPHIC COVERAC VIDEO No STILLS No

33. SPECIAL INSTRUCTIONS

The quardricyclane was obtained from WSTF No. 96-29649 and the nickel was obtained from WSTF No. 92-25979.

JSC FORM 2035

APPENDIX F

WSTF 96-29652
8 March 1996

MATERIALS COMPATIBILITY TESTS: EFFECTS OF NARLOY Z ON THE VALENCE ISOMERIZATION OF QUADRICYCLANE BY ACCELERATING RATE CALORIMETRY SPECIAL TEST DATA REPORT

NASA WHITE SANDS TEST FACILITY

MATERIALS COMPATIBILITY TESTS: EFFECTS OF NARLOY Z ON THE VALENCE ISOMERIZATION OF QUADRICYCLANE BY ACCELERATING RATE CALORIMETRY SPECIAL TEST DATA REPORT

WSTF # 96-29652
March 8, 1996

1.0 INTRODUCTION

The NASA White Sands Test Facility (WSTF) was requested by Phillips Laboratory/ Hughes STX to investigate thermal hazards associated with quadricyclane (quadricyclo[2.2.1.$0^{2,6}$.$0^{3,5}$]heptane). Quadricyclane is a high energy, high density compound which exothermically isomerizes to norbornadiene (bicyclo[2.2.1]hepta-2,5-diene). The high heat of formation of quadricyclane ($\Delta H_f^o{}_{(g)}$ = 339 kJ mole^{-1}) suggests its use as an additive to liquid hydrocarbon propellants.

The isomerization of quadricyclane to norbornadiene is known to be catalyzed by transition metal compounds. This catalysis raises compatibility issues, particularly with the ferrous- and copper-based alloys used in propellant systems.

WSTF has broad experience in the study of propellant system materials compatibility and thermal hazards based on the technique of accelerating rate calorimetry (ARC). WSTF has published manuals containing the results of hydrazine and monomethylhydrazine ARC studies.[1,2]

2.0 OBJECTIVE

Determine the effect of Narloy Z turnings on the isomerization rate of quadricyclane using an accelerating rate calorimeter.

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[1] Pedley, M. D., D. L. Baker, H. D. Beeson, R. C. Wedlich, F. J. Benz, R. L. Bunker, and N. B. Martin. *Fire, Explosion, Compatibility, and Safety Hazards of Hydrazine*. RD-WSTF-0002, February 20, 1990.

[2] Woods, S. S., D. B. Wilson, R. L. Bunker, D. L. Baker, and N. B. Martin. *Fire, Explosion, Compatibility, and Safety Hazards of Monomethylhydrazine*. RD-WSTF-0003, May 5, 1993.

NASA WHITE SANDS TEST FACILITY

MATERIALS COMPATIBILITY TESTS: EFFECTS OF NARLOY Z ON THE VALENCE ISOMERIZATION OF QUADRICYCLANE BY ACCELERATING RATE CALORIMETRY SPECIAL TEST DATA REPORT

WSTF # 96-29652
March 8, 1996

3.0 TEST MATERIALS

Test Material Name:	Narloy Z
WSTF Material Number:	86-19817
Chemical Class:	Alloy
Specific Surface Area:	0.011 m^2/g
Appearance:	Copper Turnings

Test Material Name:	Quadricyclane
WSTF Material Number:	96-29649
Vendor Name:	Aldrich Chemical Co.
Address:	P.O. Box 14508, St. Louis, MO 63167
Lot Number:	MZ029025JL
Chemical Class:	Organic Compound
Appearance:	Clear liquid

4.0 TEST DOCUMENT

JSC Form 2035 (Appendix)

5.0 EXPERIMENTAL APPROACH

A commercial accelerating rate calorimeter (Columbia Scientific Industries, Austin, TX) was used to determine the isomerization rate of quadricyclane.

The calorimeter consists of an insulated chamber that surrounds the reaction vessel. The reaction vessel is a 2.54-cm- (1-in.-) diameter sphere made of commercially pure titanium with a volume of 9 mL. The calorimeter is divided into separate zones that are individually temperature controlled using thermocouples, cartridge heaters, and a microprocessor. A thermocouple is also attached to the reaction vessel.

Before use, the reaction vessel was cleaned in a two-step process. First, the vessel was cleaned with detergent and aqueous sodium hydroxide and rinsed with tap water. Next, the vessel was cleaned with a phosphoric acid/2-butoxyethanol solution and rinsed with tap water followed by a deionized water rinse. Finally, the vessel was dried with gaseous nitrogen. The clean reaction vessel was fitted with a stainless steel 316L ferrule and plug and was weighed at 24 g. The reaction vessel was then loaded with 1.0 g of metal sample, purged with nitrogen, charged with 1.0 mL of quadricyclane, sealed with the plug, and reweighed. Next, the reaction vessel was shaken to wet all internal surfaces with quadricyclane, connected to a thermocouple, and suspended in the ARC. The ARC experiment was then initiated. At the completion of the test, the reaction vessel was cooled and reweighed as a check for leaks. Testing was repeated until three reproducible tests were obtained.

The surface area of the Narloy Z turnings was determined using a Flowsorb II 2300 (Micromeritics) with a gas mixture of 0.0337 percent krypton in helium. The Narloy Z turnings had a specific surface area of 0.011 $m^2\ g^{-1}$. The surface area of a reference powder was measured immediately before that of the sample.

6.0 EXPERIMENTAL RESULTS

Time-temperature data for the thermal isomerization of quadricyclane in the presence of Narloy Z turnings were analyzed using a thermokinetic model developed at WSTF. Log(rate) vs inverse temperature plots of three runs are shown in Figure 1.

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Activation parameters for use in the Arrhenius equation:

$$k = Ae^{(-Ea/RT)}$$

where k is the first-order rate constant(sec^{-1}) for the isomerization of quadricyclane to norbornadiene, A is the pre-exponential term, Ea is the activation energy (kJ $mole^{-1}$), R is the universal gas constant (8.314×10^{-3} kJ $mole^{-1}$), and T is the absolute temperature (K) were calculated over the temperature range 411 to 467 K. The activation parameters for the isomerization reactions are given in Table 1.

Under the standard test conditions used at WSTF, the average onset temperature for the isomerization of quadricyclane with no added metal is 417 K. However, the onset temperature is system dependent and does not imply that isomerization always begins at that temperature. Using WSTF test conditions, the average onset temperature in the presence of Narloy Z is 411 K.

Table 1. Activation Parameters for Quadricyclane Isomerization with Narloy Z

Number	A (sec^{-1})	Ea (kJ $mole^{-1}$)
Quad 2042	3.6×10^{13}	146.1
Quad 2043	4.2×10^{14}	155.1
Quad 2044	5.8×10^{13}	147.6
Average	$1.7 \pm 0.8 \times 10^{14}$	149.6 ± 1.7

The average activation parameters were calculated from the mean rate at each temperature as a function of temperature and are presented with estimated standard errors. From the averaged activation parameters, the reaction rate at 415 K was calculated to be 1.5×10^{-7} mole sec^{-1}. Using the value of -91.5 kJ $mole^{-1}$ for the vapor phase heat of isomerization, the heat generation rate was calculated to be -1.4×10^{-5} kJ/sec^{-1}. The rate at 415 K in the absence of added Narloy Z was calculated to be 8.6×10^{-8} mole sec^{-1}. The isomerization is 1.8 times faster in the presence of Narloy Z relative to the reaction rate in the absence of Narloy Z.

7.0 TEST SUMMARY

The effect of Narloy Z on the isomerization rate of quadricyclane was determined using ARC. The Arrhenius activation parameters, A and Ea, were calculated and reported. The rate of isomerization was found to be 1.5×10^{-7} mole sec^{-1} at 415 K which is 1.8 times that of the isomerization in the absence of 0.01 m^2 of Narloy Z.

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SPECIAL TEST DATA REPORT

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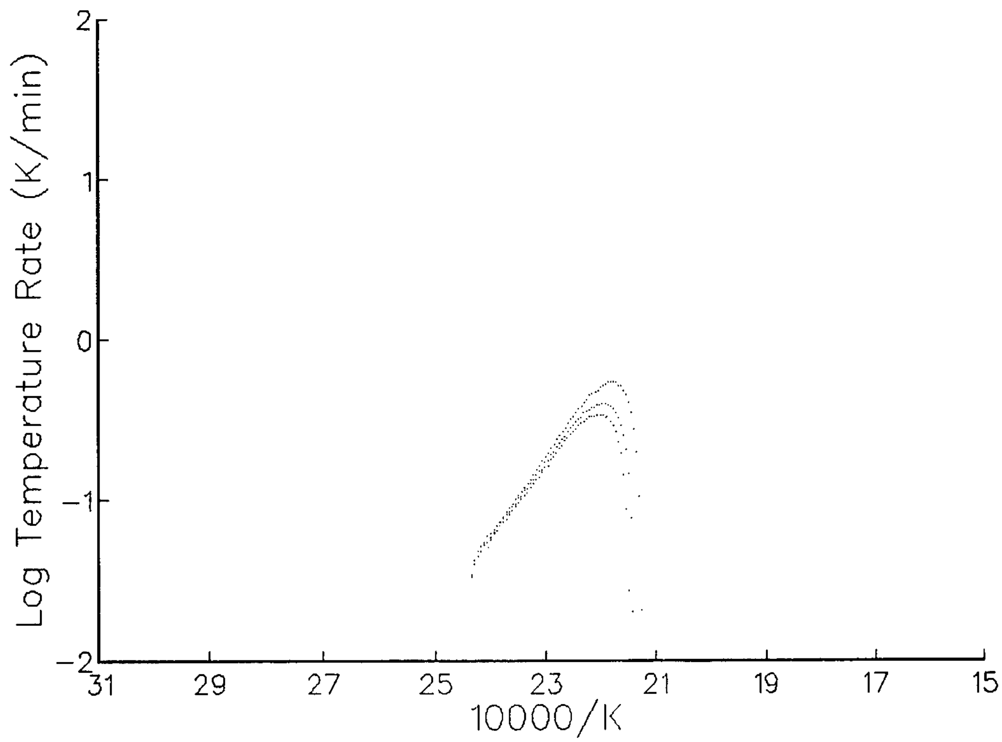

Figure 1. Test Results for Runs Quad2042, Quad2043, and Quad2044

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APPENDIX

JSC Form 2035

NASA JSC TEST REQUEST

NOTE TO TEST FACILITY: A COPY OF THIS REQUEST SHOULD BE RETURNED WITH THE TEST REPORT.

OFFICE USE ONLY	
TEST FACILITY I.D. NUMBER	96-29652
COORDINATOR	DB
REQUESTNO.	WSTF
TEST FACILITY	WSTF
CODE	

NAME	Angelica Wilson/Dave Baker
ORGANIZATION	OL-AC PL/RKF NASA/RF
ADDRESS	Phillips Laboratory/Hughes STX 10 E. Saturn Blvd. Edwards AFB, CA 93524 White Sands Test Facility Las Cruces, NM 88004
DATE	January 02, 1996
PHONE	(805) 275-5317/(505) 524-5605
1. MANUFACTURER'S IDENTIFICATION (ITEM DESCRIPTION)	Narloy Z w/Quadricyclane
2. MANUFACTURER'S NAME	Aldrich Chemical Co. P.O. Box 14508 St. Louis, MO 63167
3. SPECIFICATION	
4. CHEMICAL CLASS	
5. GENERIC USE	
6. CHECK CATEGORY NHB 8060.1 A, B, C	NHB 8060.1C
7. TEST REQUIRED 1 THROUGH 18, VCM, TQCM, SPECIAL	Special-Accelerated Rate Calorimetry
8. VEHICLE	
9. PART NUMBER/SERIALNO.	
10. PROJECT	ARC Quadricyclane
11. USE TEMPERATURE	
12. USE ATMOSPHERE/FLUID	
13. IGNITER TYPE	
14. USE PRESSURE	
15. USE THICKNESS	
16. INTENDED APPLICATION	
17. QTY IN HABITABLE AREA/HAZARDOUS FLUID/VACUUM	
18. CURE TIME	
19. CURE TEMPERATURE	
20. CURE PRESSURE	
21. TEST ARTICLE WT.	
22. TEST ARTICLE AREA	
23. NUMBER OF ITEMS TESTED	
24. NO. OF ITEMS TO BE FLOWN	
25. TEST CHAMBER VOLUME	
26. TEST CHAMBER ATMOSPHERE	
27. TEST CHAMBER PRESSURE	
28. TEST CHAMBER TEMPERATURE	
29. TEST CHAMBER DURATION	
30. CLEANING SPEC	
31. MATERIAL CODE	
32. PHOTOGRAPHICCOVERA[GE]	VIDEO: No; STILLS: No

33. SPECIAL INSTRUCTIONS

The quardricyclane was obtained from WSTF No. 96-29649 and the Narloy Z was obtained from WSTF No. 86-19817.

JSC FORM 2035